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BLEACHING POWDER

AND ITS

ACTION IN BLEACHING.

Original Memoirs by R. L. TAYLOR, F.I.C.

ISSUED AND EDITED BY THE AUTHOR.

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PREFACE.

At various times I have been urged, by Dr. E. Knecht and other friends, who seem to think that some of my contributions to the Theory and Practice of Bleaching, and to the discussion as to the constitution and properties of Bleaching Powder, were of some value, to publish an account of them in book form. It was pointed out to me that, scattered as these contributions are among various numbers of the journals of the Chemical Society and of the Society of Dyers and Colourists, they are not easily accessible, especially to the younger generation of students interested in bleaching.

My first idea was simply to write, as far as possible in a connected form, an account of my experiments and conclusions, and publish this as a short Monograph on Bleaching and Bleaching Powder. But, as this would have involved, in any case, many copious quotations from the various papers, I have decided that it would be simplest, and I hope not less useful, to reprint the papers practically as they appeared when they were first published, with merely such alterations as I considered necessary or desirable.

The papers are arranged in the order in which they first appeared. They represent more than a dozen years' work, which could only be carried on intermittently when other duties permitted. All the papers except one represent experimental work done by myself. In that one (Number III. in the present issue), I had the valuable assistance of Mr. Clifford Bostock, who was then a Research Student in the Manchester College of Technology. A few years afterwards Bostock was killed in the war. His was one of the many instances of a promising career cut short by that calamity.

R. L. T.

Manchester, 1922.

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I.

RESEARCHES ON BLEACHING POWDER.
PART I.

(From the *Transactions of the Chemical Society*, 1910. Vol. 97).

FOR the purpose of this investigation, it was first of all necessary to devise a method for distinguishing between pure chlorine and hypochlorous acid, and, in a mixture of the two, finding their proportions.

The method used was to pass the gases through a known volume of $N/10$-sodium arsenite. The action of chlorine and of hypochlorous acid on sodium arsenite may be represented thus:

$$(1)\ As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl.$$
$$(2)\ As_2O_3 + 2HOCl = As_2O_5 + 2HCl.$$

It is plain that, for the same amount of arsenite oxidised, twice as much hydrochloric acid (or chloride) is produced in the case of chlorine as in the case of hypochlorous acid. The arsenite (which must always be in excess, so that it is not completely oxidised) is then divided into two equal parts. In one half, the amount of arsenite remaining unoxidised is determined by means of $N/10$-iodine solution, and from this the amount oxidised is ascertained. In the other half, the amount of chlorine is determined by means of $N/10$-silver nitrate. In the latter determination the use of an indicator was very soon discarded, although, if a considerable proportion of the arsenite has been oxidised, the arsenate produced acts fairly well as an indicator, and may be used instead of adding a chromate to the solution. Much more trustworthy results, however, are obtained by acidifying the solution with nitric acid, adding a little of the silver solution, boiling for a minute or two, and then filtering a portion of the liquid. A little more of the silver solution is added, drop by drop, to the filtered portion, which is then returned to the bulk, and this boiled and filtered again. This is continued until the filtered portion gives no further precipitate with the silver solution. As described, the process seems tedious, but in practice it works very well, and the determination of the chlorine can be made fairly rapidly. In this process, as the solutions used are all decinormal, and therefore equal to each other, when the oxidising agent is pure chlorine, the amount of silver nitrate used (= amount of chloride present) is the same as the amount of arsenite oxidised. When hypochlorous acid is the oxidising agent, the chloride produced is only half the amount of arsenite oxidised.

The Action of Carbon Dioxide on Bleaching Powder.

It is very frequently stated, and probably usually considered, that carbon dioxide simply liberates hypochlorous acid from bleaching powder. A considerable number of observers, however, have pointed out that chlorine is produced when pure carbon dioxide acts on bleaching powder.

Thus, Richards and Juncker (*Dingl. Polyt. J.*, 1874, 211, 31) state that dry bleaching powder is almost undecomposed by carbon dioxide. If about 10 per cent. of water is present, both chlorine and hypochlorous acid are produced.

Wolters (*J. pr. Chem.*, 1874, [ii.], 10, 128) refers to the liberation of chlorine by the action of carbon dioxide on bleaching powder, and Lunge and Schappi (*Dingl. Polyt. J.*, 1889, 273, 63) state that carbon dioxide expels nearly the whole of the chlorine from bleaching powder.

Dreyfus (*Bull. Soc. chim.*, 1884, [ii.], 41, 600) found that carbon dioxide has no action on calcium chloride, but, in the presence of chlorine monoxide, either dry or in aqueous solution, it liberates chlorine.

More recently this question, with others relating to bleaching powder, has been investigated by von Tiesenholt (*J. pr. Chem.*, 1901, [ii.], 63, 30; 1902, [ii.], 512; 1906, [ii.], 73, 301). Some of his conclusions will be referred to later.

In my first experiments, carbon dioxide, in its ordinary moist condition, after being well washed with water, was passed through a U-tube containing bleaching powder and a sufficient amount of glass wool to give a free passage for the gas. Carbon dioxide, as ordinarily prepared by the action of hydrochloric acid on marble, invariably carries with it a little hydrochloric acid, and, in some of the experiments, this was removed by passing the gas through glass wool wetted with a solution of silver nitrate, which acts quite effectually. When, however, the gas is well washed with water, the amount of hydrochloric acid accompanying it is not sufficient to seriously affect the results. After passing through the bleaching powder, the gas was passed through a Bunsen U-tube containing $N/10$-sodium arsenite.

A considerable number of experiments were made, and the following is an example of the results invariably obtained. Twenty c.c. of the $N/10$-arsenite were used.

I

Amount of arsenite oxidised	8.35 c.c.
Amount of $N/10$-silver nitrate used	8.4 c.c.

It is plain from this that the sole product of the action of carbon dioxide on bleaching powder is chlorine. The escaping gas has a strong odour of chlorine, and none at all of hypochlorous acid. The action proceeds very rapidly if the carbon dioxide is quite moist.

In some further experiments, the carbon dioxide was dried by passing it over calcium chloride. The effect of drying the gas is that the action becomes much slower, and, as the moisture usually present in the bleaching powder is gradually carried away by the dry carbon dioxide, it soon becomes extremely slow. When this point has been reached, the instantaneous acceleration of the action when the drying tube is removed is very striking. The following three experiments show that the product is the same with the dry as with the moist gas, namely, nothing but chlorine.

II

I	Arsenite oxidised.	Chloride produced.
1	3.4	3.5
2	1.9	1.95
3	6.55	6.65

The slight excess of silver nitrate used may have been due to a little hydrochloric acid carried over, although the actual amounts are not beyond the limits of accuracy of the method.

When carbon dioxide is passed through a solution of bleaching powder in water, the action is very rapid, but the result is exactly the same, as the following experiments show :

III.

	Arsenite oxidised.	Chloride produced.
1	5·6	5·58
2	3·1	3·1

The issuing gas again has a strong odour of chlorine, and none at all of hypochlorous acid.

Action of Carbon Dioxide on a Mixture of Sodium Chloride and Hypochlorite, and on a Mixture of Bromide and Hypobromite.

The mixture of sodium chloride and hypochlorite was prepared by passing chlorine into a moderately concentrated cold solution of sodium hydroxide. The following experiments show that the action is exactly the same as with a solution of bleaching powder :—

IV.

	Arsenite oxidised.	Chloride produced.
1	4·1	4·12
2	6·1	6·13

When carbon dioxide is passed through a solution containing a mixture of a bromide and a hypobromite there is, as one would naturally expect, an immediate and copious liberation of bromine.

It is well known that carbon dioxide acts in a similar way on a mixture of iodide and hypoiodite.

It appears, from the foregoing experiments, that the action of carbonic acid on bleaching powder and similar substances is like that of any other acid. There has been much discussion as to the actual constitution of dry bleaching powder, but, whatever that constitution may be, it may be taken that, in solution or in presence of water, it is, to all intents and purposes, a mixture of chloride and hypochlorite. The usual explanation of the action of, say, sulphuric acid (when used in considerable quantity) on bleaching powder is that the chloride and hypochlorite are both decomposed, with the simultaneous production of hydrochloric and hypochlorous acids, and that these decompose each other, with the liberation of chlorine. The question is whether or not we must seek for some other explanation of the action of carbonic acid. For my part I have no doubt as to the answer to that question—the action of carbonic acid on bleaching powder is exactly like that of other acids. Of course, this involves the conclusion that calcium chloride (or sodium chloride, for example) is decomposed, when in solution, by carbonic acid, with the liberation of hydrochloric acid, and that, therefore, the action of hydrochloric acid on carbonates is a reversible one :

$$CaCO_3 + 2HCl \rightleftharpoons CaCl_2 + H_2CO_3.$$

I have tried to obtain some experimental evidence that this is the case, and not altogether without success.

Many years ago Müller (*Journ. Chem. Soc.*, 1870, 23, 36) stated that a solution of lead chloride is decomposed when carbon dioxide is passed through it, with liberation of hydrochloric acid and precipitation of a chlorocarbonate, and that some of the liberated acid could actually be distilled off. He also stated that carbon dioxide, under considerable pressure, would decompose sodium and calcium chlorides, when in solution in water, with liberation of hydrochloric acid. He used ultramarine as an indicator, and stated that, whilst carbon dioxide alone does not decompose ultramarine suspended in water, even under considerable pressure, if the water contains common salt dissolved in it the colour of the ultramarine is destroyed.

I am unable to confirm the latter observation. Carbon dioxide, when bubbled through water in which a little ultramarine is suspended, has no effect on it, whether the water contains salt or not. Under a pressure of a few atmospheres, however, ultramarine is decomposed and decolorised by carbonic acid alone, and I have been unable to observe any difference in the action when the water contained salt as well. The experiments I made were performed in an ordinary sparklet apparatus, in which the pressure attains five or six atmospheres. If distilled water with a little ultramarine suspended in it is placed in such an apparatus, and then the liquid charged with carbon dioxide in the usual way, there is no immediate effect, but, in the course of a day or two, the colour of the ultramarine gradually disappears. As stated above, the presence of salt (or of calcium chloride) in the water makes no apparent difference in the result.

Methyl-orange is, however, a much more delicate indicator for acids than ultramarine. It is usually assumed that the former is not affected by carbonic acid, but this is not quite correct. If well washed carbon dioxide is bubbled through distilled water containing a little methyl-orange, there is a distinct alteration of the colour, although it does not turn pink. If, however, the water contains also a little pure salt, or calcium chloride, or potassium chloride, the colour becomes distinctly pink when the carbon dioxide is bubbled through. The change of colour is most striking in the case of the common salt, but it is quite evident with the other chlorides. This may be taken as evidence that carbonic acid liberates a sensible amount of hydrochloric acid in solutions of chlorides, that is to say, the action of hydrochloric acid on carbonates is a reversible one. Of course, the amount of hydrochloric acid thus liberated must be extremely small, but it will be quite sufficient to explain the action of carbonic acid on bleaching powder and similar substances. The small amount of hydrochloric acid liberated will be at once decomposed by the hypochlorous acid liberated simultaneously from the hypochlorite; this will enable the action of the carbonic acid to proceed as before, and so there will be a continuous evolution of chlorine, and, if this is carried away as fast as it is formed, the bleaching powder will be almost completely decomposed.

It may here be noted that if carbon dixoide is bubbled through water containing potassium bromide or ammonium chloride and coloured with methyl-orange, the change of colour is not so striking as in the case of the three chlorides mentioned above. Pure water coloured with methyl-orange becomes quite pink when charged with carbon dioxide in a sparklet apparatus.

Von Tiesenholt (*loc. cit.*) explains the production of chlorine when carbon dioxide acts on bleaching powder by supposing that hypochlorous acid is first formed by the action of the carbon dioxide on the hypochlorite present, and that this acts on the calcium chloride, liberating chlorine:

$$CaCl_2 + 2HOCl = Ca(OH)_2 + 2Cl_2.$$

He finds, in confirmation of this view, that chlorine is liberated when a solution of hypochlorous acid is added to calcium chloride or to common salt. The experiments here described, however, show that nothing but chlorine is produced by the action of carbonic acid on bleaching powder, so that all the hypochlorous acid which is liberated must be decomposed. Apparently, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a sufficient amount of a chloride, so that it would be impossible to expel any hypochlorous acid from a solution which contains chlorides. As will be seen later, however, mixtures of chlorine and hypochlorous acid containing a considerable proportion of the latter can be expelled from solutions of bleaching powder. Consequently, whilst it is possible that the action of hypochlorous acid on chlorides may account for some of the chlorine which is produced in the case of concentrated solutions or the merely moist bleaching powder for example, von Tiesenholt's explanation would not appear to be preferable to the one offered above.

The Action of Air on Bleaching Powder.

Although this was not the order in which the experiments were actually tried, it will be best to describe first the effect of air from which all the carbon dioxide has been removed. This was done by passing the air through washing cylinders containing coke wet with a concentrated solution of sodium hydroxide. It was then bubbled through a milky solution of bleaching powder (about 5 to 10 per cent), and afterwards through solution of sodium arsenite.

In all the experiments with air, it was passed through at a rate of about 10 to 15 litres per hour.

Air free from carbon dioxide is practically inert so far as bleaching powder is concerned, and naturally all that it can do is to sweep out any chlorine or hypochlorous acid which may happen to be present. Consequently, the action is very slow, and the experiments had to be carried on for a long time (from 72 to 96 hours) in order to obtain sufficient oxidising action in the solution of arsenite to be able to judge what was being carried over. The following results were obtained in three separate experiments:—

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
[illegible]	1·08	0·57	90	10
2	1·0	0·45	100	0
3	0·8	0·38	100	0

The amount of oxidation in these experiments was very little, but they appear to show that a small amount of free hypochlorous acid exists in a solution of bleaching powder, which is simply swept out by the passage of air free from carbon dioxide through it. Probably the free hypochlorous acid is due to the calcium hypochlorite in a dilute solution being to some extent hydrolysed, thus:—

$$Ca(OCl)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HOCl.$$

This doubtless accounts for the fact that solutions of bleaching powder have an odour of hypochlorous acid.

One similar experiment to the above was made in which the solution of bleaching powder was kept at a temperature of about 40° the whole of the time. In this experiment, also, practically nothing but hypochlorous acid was swept out, the only difference being that, as one would expect, the time required was rather less.

Action of Ordinary Air on Bleaching Powder.

A considerable number of experiments were made with ordinary air, passing it through a tube containing dry bleaching powder, and then through the solution of arsenite. At first the action is rather slow, but, as the bleaching powder gradually becomes wet, the action proceeds more and more rapidly. In some of the experiments the moisture of the air was purposely increased by passing it through a tube containing wet glass wool. In each of the two following series of experiments the same tube of bleaching powder was used throughout. The time occupied by each experiment varied from about 24 hours at the beginning to six hours when the bleaching powder had become wet:

VI.

SERIES I.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	4·54	4·0	11	89
2	2·9	2·56	13	87
3	2·55	2·3	10	[illegible]
4	7·0	6·95	0	100
5	7·9	7·95	0	100

SERIES 2.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	2·1	1·83	15	85
2	3·35	3·1	8	92
3	6·0	6·05	0	100

The above experiments are selected from a considerable number, and they all tend to show that, at the outset, ordinary air sweeps out from bleaching powder a mixture containing from 80 to 90 per cent of chlorine, and from 10 to 20 per cent of hypochlorous acid, but that, as the action proceeds, the amount of hypochlorous acid gradually diminishes, and at last nothing but chlorine appears. The gradation of the experiments is not the same in the two series, but that is partly due to the fact that some intermediate experiments in both series were spoiled by going on too long.

When ordinary air is passed through a solution of bleaching powder (not filtered, and containing about 5 to 10 per cent of the powder), the proportion of hypochlorous acid swept out is considerably greater, as indeed one would expect if we accept the suggestion that the hypochlorous acid is due to hydrolysis of the calcium hypochlorite. As in the case of the dry powder, however, the amount of hypochlorous acid gradually diminishes as the experiment proceeds, although it does not disappear altogether. The following experiments were made with the same solution of bleaching powder, in the order in which they are given. In Experiment No. 4, the proportion of hypochlorous acid appears to have risen slightly, but the method of determining it is not accurate enough to enable one to say that the amounts in Experiments 3 and 4 were not substantially the same. The action was very slow in the first experiment, but much more rapid afterwards :—

VII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	4·48	2·94	52	48
[illegible]	9·15	7·27	25	75
3	3·18	2·88	10	90
4	3·34	2·87	16	84

It must be pointed out that the above numbers, showing the relative amounts of hypochlorous acid and chlorine swept out of the liquid by the air, do not necessarily represent the actual proportions present at any moment in the liquid itself. There is no doubt that chlorine, being less soluble in water than hypochlorous acid, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the above numbers indicate.

These results, showing the action of ordinary air on bleaching powder, are very remarkable. The difference between the action of ordinary air and air from which the carbon dioxide has been removed is, at first sight, almost incredible. Whereas the latter simply sweeps out from a solution of bleaching powder (although very slowly) practically pure hypochlorous acid, the presence of the really very small amount of carbon dioxide which usually exists in ordinary air causes the action to proceed much more rapidly (although not with anything like the rapidity with which pure carbon dioxide acts), and, after a time, has almost the same effect, so far as the product is concerned, as passing pure carbon dioxide through it.

I have already expressed the opinion that the action of pure moist carbon dioxide on bleaching powder is the same as that of other acids—it is a mass action, and the carbonic acid decomposes both the chloride and the hypochlorite. Whilst one may accept this explanation in the case of pure carbon dioxide used in comparatively large quantities, and always locally in large excess, it is impossible to believe that the small amount of carbon dioxide present in ordinary air can act in the same way. We must, therefore, look for some other explanation.

The Action of Chlorine on Alkalis a Reversible Action.

In former papers (*Mem. Manchester Phil. Soc.*, 1897, 41, No. VIII.; *Journ. Chem. Soc.*, 1900, 77, 725) I have pointed out that the action of iodine on alkalis is a reversible one. If an alkali is added to a solution of iodine in water or in potassium iodide until the colour just disappears, the addition of potassium iodide to the solution causes the liberation of some of the iodine:—

$$2KOH + I_2 \rightleftharpoons KI + KOI + H_2O.$$

The addition of the extra amount of potassium iodide causes the reaction to proceed from right to left in the above expression.

Also, and this, too, follows from the fact that the action is reversible, the amount of alkali needed to complete the reaction from left to right and to remove the colour of the iodine is considerably more than is required by the equation, so that the almost colourless solution of iodide and hypoiodite always contains some free alkali.

When these experiments were made, similar ones were also performed with bromine and alkalis, but analogous results were not obtained. The reason of this must have been that too strong a solution of bromine was used, because I find that the reversibility of the action of bromine on alkalis is quite as striking as that of iodine if a very dilute solution of bromine is employed. The action is not nearly so easy to see with ordinary bromine water, but if this is diluted with 10 to 20 times its bulk of water, and then sodium or potassium hydroxide added drop by drop until the colour of the bromine has disappeared, the addition of a little concentrated solution of potassium bromide causes a manifest liberation of bromine. The liberation of bromine is seen still more plainly if, instead of the solution of potassium bromide, a considerable amount of the powdered salt is added. The addition of the extra potassium bromide causes the action to proceed from right to left :

$$2KOH + Br_2 \rightleftarrows KBr + KOBr + H_2O.$$

It is perfectly reasonable to suppose, then, that the action of chlorine on alkalis is also a reversible action. This has already been suggested by von Tiesenholt (*loc. cit.*), who describes a number of experiments which point to this conclusion. I have been able to demonstrate, by experiments which are described later, that this conclusion is correct, and it will be seen that it supplies a perfectly satisfactory explanation of the action of ordinary air on bleaching powder, and that it also explains some well-known facts with regard to some bleaching solutions which have been hitherto apparently inexplicable.

If we represent the action of chlorine on sodium hydroxide and on slaked lime thus :

$$2NaOH + Cl_2 \rightleftarrows NaCl + NaOCl + H_2O$$

and

$$2Ca(OH)_2 + 2Cl_2 \rightleftarrows CaCl_2 + Ca(OCl)_2 + 2H_2O$$

---

* It is not suggested that this equation represents what actually occurs in the manufacture of bleaching powder, but simply the condition of equilibrium in which it exists when wet or in solution.

It is plain that the chlorides produced by the action are continually tending to reverse the reaction, so that, to carry it to a finish from left to right, there must always be a considerable amount of free sodium hydroxide or lime present. It is a well-known fact that bleaching powder always contains a considerable amount of free lime, and that it is impossible to prepare it otherwise. If this free lime, or a portion of it, is removed, then the reaction will proceed in the opposite direction to a greater or less extent, and chlorine will be liberated.

A number of experiments were made to test this point. A filtered solution of bleaching powder was employed, having a specific gravity of 1·03 to 1·06 in different experiments. In order to remove some of the free lime, the solution was exposed to air for some hours in a shallow dish, with occasional shaking. The amount of free lime present in such a solution is considerable, and the latter becomes very milky on exposure to air. The liquid was filtered from the precipitated calcium carbonate, and air free from carbon dioxide was passed through it and into the arsenite solution in the usual way. The following are some of the results obtained :—

VIII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	4·0	3·16	26	74
2	3·8	3·0	27	73
3	2·6	1·8	44	56
4	5·92	5·15	15	85
5	4·35	4·04	8	92
6	2·27	1·52	50	50

Most of the separate experiments were made with different portions of the solution, which had been exposed to air for different lengths of time, so that the extent to which the free lime was removed varied. Doubtless this accounts for the irregularity in the results. In all the above experiments the action was much more rapid than was the case with the solution from which none of the free lime had been removed (see Exps. V., p. 11), the rapidity evidently depending on the extent to which this removal had been carried. It will be noted that besides the large quantities of free chlorine produced, in most of the experiments the amount of hypochlorous acid swept out from the liquid was very much greater than was the case with the solution from which no free lime had been removed. This is quite what one would expect to occur. The hypochlorous acid, as before stated, is probably due to hydrolysis of the calcium hypochlorite in the solution. This also is a reversible action, and as one of the products of the hydrolysis is free lime, the removal of the lime naturally stimulates this action as well.

These experiments demonstrate quite sufficiently the reversibility of the reaction between chlorine and calcium hydroxide. As the free lime is more or less removed, the reaction proceeds in the opposite direction, and chlorine is liberated. In these experiments the free chlorine is swept out of the solution, but it is continually being reproduced, the steady removal of the chlorine allowing the reverse action to take place continuously. If the free chlorine were removed from the solution in any other way, by bleaching, for example, it would in the same way be continually reproduced as long as any of the bleaching substance remained. It follows from this, of course, that the bleaching action of a solution of bleaching powder will be stimulated by the removal of free lime from the solution. This will be referred to again later.

The action of ordinary moist air on bleaching powder, both solid and in solution, described on p. 12, is now perfectly intelligible. The carbon dioxide in the air combines with the free lime, and, as this gradually diminishes and finally practically disappears, the reverse action proceeds freely, and, of course, chlorine is produced.*

It is usually understood, and has been frequently stated, that a pure solution of hypochlorous acid bleaches more energetically and more rapidly than free chlorine. It may be doubted whether this is really the case. I have prepared practically pure solutions of hypochlorous acid, and compared its action with that of a solution of chlorine on various colouring matters, and I have failed to find any evidence of the greater activity of hypochlorous acid. Rather the contrary. With a solution of indigo-carmine, for example, the bleaching action of chlorine is much more rapid than that of hypochlorous acid—in the case of the latter the action is to be described as sluggish, rather than rapid. This is an important point, because I am strongly of opinion that in the use of solutions of bleaching powder and similar substances for bleaching purposes, most of the actions generally attributed to hypochlorous acid are really due to chlorine, and that, in practice, hypochlorous acid plays only a minor part in bleaching.

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* It may be asked, if the removal of free lime by carbon dioxide is a satisfactory explanation of the fact that ordinary air expels chlorine from bleaching powder, would not this also explain the action of pure carbon dioxide on bleaching powder, so that there would be no need to assume, as is done in the first part of this paper, that carbonic acid decomposes chlorides with the liberation of hydrochloric acid? The author adheres to the latter explanation simply because the action of carbon dioxide is so much more rapid than that of air. A stream of carbon dioxide through a solution of bleaching powder liberates chlorine from 10 to 20 times more rapidly than air at its quickest, and the action altogether suggests a rapid and complete decomposition, such as is effected by other acids, rather than the mere sweeping out of chlorine produced by the reversed action.

It is remarkable how the bleaching action of a solution of bleaching powder is stimulated by the mere removal of the free lime in it. If a strip of Turkey-red calico is placed in a clear solution of bleaching powder so that it is completely immersed in the liquid, and if the liquid is kept in a closed vessel so that air has no access to it, there is scarcely any bleaching action at all, even after several days. If, however, the solution is placed in a basin or a shallow dish, so that air has free access, and if a small portion of the red calico is left outside the liquid, so that it is reached by the solution and the air at the same time, the portion outside is bleached quite rapidly. Further, if the coloured calico is completely immersed in a little of the solution contained, say, in a deep test-tube, and the test-tube is breathed into about half-a-dozen times, shaking each time, the calico is very soon bleached. Also, whilst, as stated above, a fresh solution of bleaching powder has very little, if any, bleaching action on a piece of red calico completely immersed in it, if the solution has been exposed to air in a shallow dish for a few hours, with occasional shaking, then a piece of red calico completely immersed in it is bleached rapidly.

A simple but very striking experiment which illustrates the same point is to immerse a strip of ordinary red litmus paper in a fresh solution of bleaching powder. The paper is turned blue, and in a short time it is bleached. If, however, immediately after it has been dipped in the solution, it is breathed upon, it is bleached almost instantly. A solution of bleaching powder which has been well exposed to air, as described above, bleaches litmus paper at once.

In all these cases the more rapid bleaching action is simply due to the removal of free lime, and I think it is plain, also, if reference is made to the experiments, Series VIII., on p. 16, that the principal bleaching agent is chlorine, and not hypochlorous acid. Certainly those experiments show that in some cases a considerable proportion of hypochlorous acid is swept out, but in all cases the rapidity of the bleaching action is roughly proportional to the extent to which the free lime is removed, and the more completely that is done the greater is the proportion of chlorine liberated.

It is a fact, well known in bleach-works, that an old vat is more active than a new one. The reason for this is obvious. Exposure to air, especially if the liquid is frequently stirred, gradually causes the removal of the free lime.

If the action of chlorine on lime is, as I think the above experiments sufficiently demonstrate, a reversible action, then the reverse action must be stimulated by the addition of calcium chloride to the solution. Experiments were made to see if this is the case. After Experiment No. 2 (Series VIII.) on p. 16 was finished, a considerable amount of crystallised calcium chloride was added to the same solution of bleaching powder and air free from carbon dioxide passed through it again. The action became considerably more rapid, and the effect of the calcium chloride is seen by a comparison of the two experiments. No. 1 was before, No. 2 after, the addition of the calcium chloride.

IX.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	3·8	3·0	27	70
2	4·75	4·73	0	100

The solution used in experiment No. 6 (Series VIII.) was treated in the same way with the following result:—

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	2·27	1·52	50	50
2	5·4	4·92	10	90

These experiments show plainly, that, as anticipated, the reverse action is greatly increased by the addition of more calcium chloride.

Other chlorides, of course, ought to have a similar effect. The following experiments show the effect of adding common salt to the solution. As before, the greater part of the free lime in the solution was removed by exposing it to air. Experiments 1 and 2 were successive experiments before the addition of the salt, and No. 3 shows the effect of the salt. The salt was added in considerable quantity—almost sufficient to saturate the solution.

X.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	1·75	1·4	25	75
2	5·25	4·1	28	72
3	6·53	6·55	0	100*

The addition of the salt in the above experiment caused the action to proceed much more rapidly. Thus, whilst in experiment No. 2 it took 20 hours to oxidise 5·25 c.c. of the arsenite solution, in experiment No. 3, 6·53 c.c. were oxidised in four hours, the carbon dioxide-free air passing through at approximately the same rate in both experiments.

Experiments were also made to see the effect of the addition of calcium chloride and salt to an ordinary solution of bleaching powder, without remvoing any of the free lime. The free lime in the solution, of course, tends to stop the reverse action, so that the effect of adding calcium chloride or salt to the solution is not nearly so great as when the free lime is first removed. The following is the result of the two experiments tried.

To No. 1 calcium chloride was added, and to No. 2 common salt —both in large quantity. The action proceeded very slowly indeed in both experiments, but the results are sufficient to show that, even in ordinary bleaching powder solution, the addition of chlorides has a sensible effect in reversing the action :—

---

* The apparently complete disappearance of hypochlorous acid indicated in experiments 2 (IX.) and 3 (X.) is very remarkable, and seems difficult to explain. It is not claimed, however, that the method used for determining the relative amounts of chlorine and hypochlorous acid is perfectly accurate It is doubtful whether it would be possible to determine very small proportions of hypochlorous acid by it. It must also be borne in mind (see p. 14) that chlorine is more easily swept out from the solution than hypochlorous acid, so that it is possible that the latter does not altogether disappear. Possibly, also, von Tiesenholt's explanation (see p. 10) may apply here, and the hypochlorous acid may be all decomposed by the large quantities of chlorides present in the solution.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	2·24	2·22	0	100
2	2·66	2·4	10	90

It follows from the above experiments that the addition of alcium chloride or salt to a solution of bleaching powder must xercise a stimulating effect on the bleaching action of the solution. This is actually the case. If some of the free lime has been removed from the solution, the effect of the addition of considerable amounts of calcium chloride or salt on the bleaching action is very striking. With bleaching powder solution in its ordinary state, containing the usual amount of free lime, the effect on its bleaching action of adding calcium chloride or salt is, for the reason pointed out above, not nearly so great, although it is quite sufficiently marked.

I understand that it has been found, in actual bleaching, that the addition of either calcium chloride or salt stimulates the action, but I am not aware that any satisfactory explanation of this stimulating effect has hitherto been given. It may perhaps be worth the while of practical bleachers to note that the addition of calcium chloride or salt has a much greater effect when some of the free lime has been removed—by exposing the solution to air, for example.

Bleaching solutions made by the electrolysis of a solution of salt have latterly come into considerable use, and I understand that the fact has been frequently noted that a solution of sodium hypochlorite thus prepared is more active than a solution of sodium hypochlorite, containing the same proportion of available chlorine, prepared by the addition of sodium carbonate to a solution of bleaching powder and allowing the precipitated calcium carbonate to settle. The explanation of this is obvious when it is understood that, in preparing the electrolytic bleaching solution, only a small fraction of the salt in the solution is usually decomposed. The solution thus differs from that made by the other method by containing a large amount of salt, and the effect of this is to increase the reverse action and so to liberate chlorine in the solution. Also in the electrolysis of the salt, chlorine and sodium hydroxide are produced in exactly equivalent proportions, so that there cannot be a sufficient amount of the latter to absorb the whole of the chlorine. Under these conditions, the reversing action of the excess of salt will naturally be very considerable. The greater bleaching activity of such a solution is therefore perfectly natural, and exactly what one would expect.

Summary.

1. The action of carbon dioxide on bleaching powder and similar substances results in the liberation of chlorine only—no hypochlorous acid. The conclusion is drawn that the action is like that of any other acid, and that carbonic acid decomposes both the chloride and the hypochlorite in the bleaching powder. It follows from this that the action of hydrochloric acid on carbonates is a reversible one.

2. Ordinary moist air acts on solid bleaching powder, liberating at first both chlorine and hypochlorous acid, the former in much the larger amount. After a time nothing but chlorine is produced. When ordinary air is passed through a solution of bleaching powder, a mixture of hypochlorous acid and chlorine is swept out, at first in about equal amounts; but, as the experiment proceeds, the former diminishes, and the latter increases to about 90 per cent.

3. The action of chlorine on alkalis, like that of iodine and bromine, is a reversible one, as stated by von Tiesenholt. If the free lime in bleaching powder is removed, this causes the reverse action to proceed, and thus chlorine is liberated. This explains the action of ordinary air on bleaching powder. The reversibility of the action also explains the stimulating effect on bleaching which the addition of calcium chloride or of salt causes in a solution of bleaching powder.

4. In the ordinary processes of bleaching the active bleaching agent is probably free chlorine, hypochlorous acid playing only a minor part.

II.

THE ACTION OF CHLORINE ON ALKALIS AND OF CARBON DIOXIDE ON BLEACHING POWDER.*

From the *Transactions of the Chemical Society*, 1911, Vol. 99.

In a former paper (see Paper No. I) I stated my conclusions that the action of chlorine on alkalis, like that of bromine and of iodine, is a reversible one, and that the action of carbon dioxide on bleaching powder and similar substances is like that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride.

These conclusions are controverted by S. H. Higgins (*Journ. Chem. Soc.*, 1911), and it appears to be necessary to reply to some of his criticisms.

I had pointed out that if the action of chlorine on alkalis is a reversible one, the action would be reversed either (*a*) by the removal of free alkali, or (*b*) by the addition of chlorides to the solution. I showed by actually sweeping it out from the solution that free chlorine is developed in a solution of bleaching powder (*a*) by the removal of free lime, or (*b*) by the addition of chlorides; in the latter case, however, to only a slight extent unless some of the free lime is removed first. I further pointed out that the development of free chlorine naturally stimulates the bleaching action of the solution, and described experiments showing that the bleaching action of a solution of bleaching powder or of sodium hypochlorite is much more rapid after the removal of free alkali, or on the addition of common salt or calcium chloride, provided there is not too much free alkali present.

Higgins says (1) that it is not so much the removal of the free lime from the solution as the further action of the carbon dioxide of the air on the solution after the free lime has been removed that increases the bleaching efficiency; (2) that the action of common salt and of calcium chloride in increasing the bleaching efficiency is due "to the increased attraction of the carbon dioxide of the air by the salt solution"; (3) that other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action when used in equivalent amounts.

With regard to (1) and (2) it is sufficient to point out that, in the great majority of the author's experiments, after the removal of free alkali or the addition of salt or calcium chloride to the solution, air had no access to the solution; or, when air was used, for example, for sweeping out the chlorine and hypochlorous acid in the solution, the carbon dioxide was removed from it first. Also, in the case of further experiments presently to be described, all of them were performed in closed vessels, to which air had no access. With regard to Higgins' statement (3) that "other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action," it was considered desirable that further experiments should be made.

Sodium hypochlorite solution was prepared in three different ways: (1) by passing chlorine into a cold solution of sodium hydroxide, (2) by precipitating an aqueous solution of bleaching powder with a solution of sodium carbonate, so that the filtered liquid gave no precipitate with either of the solutions, and (3) by exposing a solution of bleaching powder to air in a shallow dish for a few hours, in order to remove some of the free lime, and then precipitating as in (2).

In preparing the hypochlorite by method (1), if the chlorine is passed in too long the solution smells of free chlorine, and bleaches very rapidly, and it is desirable to add more of the alkali. This was usually done until the odour of free chlorine had disappeared, and then the solution was diluted with water until it was of such a strength as to take a reasonable time for each experiment in bleaching.

The rate of bleaching was simply the time required, in comparative experiments, to more or less completely discharge the colour of similar small pieces of turkey-red calico, previously wetted, and then immersed in the solutions.

The various solutions of hypochlorite were tried (*a*) alone, and (*b*) mixed with varying equivalent amounts of sodium chloride, sodium sulphate, and sodium nitrate. In some experiments the salts were weighed out and added in the solid state to the solutions, but more frequently measured quantities of standard solutions were used, containing respectively 117 grams of common salt, 322 grams of crystallised sodium sulphate, and 168 grams of sodium nitrate per litre.* In all such experiments the bleaching solution with which comparison was being made was diluted with water in volume equal to the amounts of the standard solutions used.

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* These solutions are 2*N*.

The results of a great number of experiments may be summarised as follows:—

I.—If the solution of the hypochlorite contains a considerable excess of free alkali, its bleaching action is extremely slow. In some experiments, when the excess of free alkali was considerable, very little bleaching occurred, even after several days. In such solutions the rate of bleaching is almost unaffected by the addition of any of the salts above mentioned. When any appreciable effect does occur, there is very little difference in the effects of the different salts used. If anything, the sodium chloride has a rather greater effect than either the sulphate or the nitrate.

II.—With solutions of hypochlorite prepared by method (1) (see above), in which only just sufficient alkali was present to prevent the odour of free chlorine in the solution, many different experiments showed that sodium chloride accelerates the bleaching action very considerably, while sodium sulphate and sodium nitrate have little or no action. In some experiments, indeed, the sodium sulphate appeared to have a distinctly retarding effect on the bleaching. The following are two experiments out of many that were tried:—

A. Five c.c. of the solution of sodium hypochlorite were used in each case. This was mixed with 5 c.c. of (*a*) water, (*b*) 2*N*-solution of sodium chloride, (*c*) 2*N*-solution of sodium sulphate, (*d*) 2*N*-solution of sodium nitrate. In (*b*) the Turkey-red calico was completely bleached in 22 minutes, whilst (*a*), (*c*) and (*d*) all took 35 minutes.

B. Same as above, but with a different solution of hypochlorite. In (*a*) the calico was bleached in 30 minutes, in (*b*) 20 minutes, in (*c*) 40 minutes, and in (*d*) 30 minutes.

III.—Sodium hypochlorite prepared by method (2) (see above), seeing that solutions of bleaching powder are always strongly alkaline, naturally will also contain a considerable amount of free alkali. The solution therefore bleaches very slowly; but if it has been very carefully prepared, so that there is no excess of sodium carbonate, it practically behaves like the solution prepared by method I.; its bleaching action is distinctly accelerated by the addition of sodium chloride, while sodium sulphate and nitrate have little or no effect. If, however, in preparing the solution, any considerable excess of sodium carbonate is used, this has almost the same effect as free alkali. The bleaching action is greatly retarded, and non of the sodium salts has any considerable effect in accelerating it.

IV.—The solution of sodium hypochlorite prepared by method (3) behaves in almost exactly the same way as that prepared by method (1); its bleaching action is greatly accelerated by sodium chloride, and hardly at all by equivalent amounts of sodium sulphate and nitrate.

As already pointed out (p. 24), all the above experiments were performed in closed vessels, so that air (other than the small amount which was already in the vessels) had no access; therefore the acceleration of the bleaching action could not have been due to carbon dioxide, as suggested by Higgins.

These additional experiments amply confirm my view as to the reversibility of the action of chlorine on alkalis.

The Action of Carbon Dioxide on Bleaching Powder.

Higgins (*loc. cit.*) also objects to my suggestion that the action of carbonic acid on bleaching powder is the same as that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride. This view would be represented by the following equations:—

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl.$

(2) $CaCl_2 + H_2O + CO_2 = CaCO_3 + 2HCl.$

(3) $2HOCl + 2HCl = 2H_2O + 2Cl_2.$

Instead of this, Higgins suggests that the action may be represented thus:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl.$

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On comparing these it is obvious that there is really very little difference between them. Higgins' equation (2) is simply a combination of my (2) and (3).

Higgins' equation (2) represents what is no doubt a complex action, and dividing it into two, as I suggest, simplifies it very considerably. As Higgins points out, the reaction is the reverse of Williamson's reaction for the effect of chlorine on water containing calcium carbonate in suspension.

$CaCO + 2Cl + H O = 2HOCl + CaCl + CO$

This also is a complex action, and doubtless takes place in two steps, the first being the action of chlorine on water (a reversible action), and the second the decomposition of calcium carbonate by hydrochloric acid

(1) $2H_2O + 2Cl_2 \rightleftharpoons 2HOCl + 2HCl$.

(2) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$.

I remember quite well that Williamson, in the 'sixties and 'seventies of last century, taught, in his lectures, that chlorine acts on water in the way represented above. He did not say in so many words that the action was a reversible one, but he probably had such a thing in his mind. He stated in his "Chemistry for Students," of which the last edition was published in 1873, that a solution of chlorine in water always contains both hypochlorous acid and hydrochloric acid, and that the presence of the latter was proved by the fact that silver chloride was precipitated from it when silver nitrate was added. There is hardly any doubt that Williamson would have offered the same explanation of the action of chlorine on water and calcium carbonate as the one suggested above.

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commercial article, as it contained more than 50 per cent of free lime.

Kopfer summarised his results as follows :—

"If to a solution of bleaching powder, or to the same substance in the dry state, a dilute mineral acid, such as nitric, hydrochloric, or sulphuric be added in such quantity as to saturate the caustic lime and to decompose the hypochlorite supposed to be present according to Gay Lussac's hypothesis, then, on distillation, an aqueous solution of almost chemically pure chlorine monoxide is obtained, which amounts in the most favourable case to about 92 per cent of the chlorine monoxide as corresponding with the theoretical hypochlorite."

Recently, one of us (see Paper I., p. 5) described a method of distinguishing between hypochlorous acid and free chlorine, and of determining the proportions of each in a mixture of the two. The method depends on the fact that, for the same amount of chlorine present, the oxidising action of hypochlorous acid is twice as great as that of free chlorine. To a mixture of the two substances an excess of sodium arsenite is added. The liquid is then divided into two equal parts; in one part the amount of arsenite oxidised is determined, and in the other the amount of chloride produced. The proportions of the two substances in the mixture can then easily be calculated.

In the present investigation the above very simple and yet fairly accurate method has been applied to a repetition of some of Kopfer's experiments, extending it also to the action of acids other than those described by him. In all these experiments the chloride present in the second half of the arsenite solution was determined by Volhard's method, which is certainly more rapid and apparently quite as trustworthy as the one described in the former paper.

The bleaching powder used for most of the experiments was a fair average sample, analysis of which gave the following figures :—

Total chlorine = 39·05 per cent.
Available chlorine = 34·63 ,,
Total lime (CaO) = 44·8 ,,
Free lime = 13·1 ,,

Assuming the bleaching powder to consist of calcium chloride and calcium hypochlorite, then 100 grams of it would contain the same effect as free alkali. The bleaching action is greatly retarded, and none of the sodium salts has any considerable effect in accelerating it.

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Higgins' equation (2) represents what is no doubt a complex action, and dividing it into two, as I suggest, simplifies it very considerably. As Higgins points out, the reaction is the reverse of Williamson's reaction for the effect of chlorine on water containing calcium carbonate in suspension.

ontain about 4·5 grams of HOCl per litre. It will be observed at with 80 or 90 c.c. of acid the distillate is much stronger, but contains a greater proportion of chlorine.

The figures representing the proportion of hypochlorous acid and lorine in the distillate are not of much value beyond the point here 70 c.c. of acid were used, because, as the amount of free lorine increases, the whole of it is not condensed in the distillate. t begins to escape about the point referred to, and, as the amount

TABLE I.

DISTILLATION WITH SULPHURIC ACID.

Volume of N-H_2SO_4, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
30	0·4	0·2	100·0	0·0
40	6·8	3·45	97·0	3·0
50	8·65	4·5	92·2	7·8
	9·15	4·75	92·6	7·4
60	16·3	8·85	84·2	15·8
	16·05	8·8	82·4	17·6
70	24·55	14·4	70·5	29·5
	24·6	14·15	73·8	26·2
80	30·65	17·55	74·6	25·4
	31·05	17·9	73·5	26·5
90	34·1	19·35	76·0	24·0
	33·4	18·8	77·7	22·3
100	24·0	14·0	71·4	28·6
	28·55	17·1	67·0	33·0
150	10·15	8·3	22·3	77·7
	10·75	8·75	22·9	77·1
200	7·05	7·25	0·0	100·0
	9·1	9·35	0·0	100·0

of acid is further increased, more and more, and finally most of it, escapes.* Therefore, in the accompanying curve, the progress of the alteration in the reaction is indicated by the gradual diminution of the amount of hypochlorous acid. These remarks apply to the cases of the other mineral acids as well.

TABLE II.

DISTILLATION WITH HYDROCHLORIC ACID.

Volume of N-HCl, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
40	4·0	2·0	100·0	0·0
50	11·25	5·8	94·0	6·0
	11·2	5·75	94·8	5·2
60	17·4	9·5	83·2	16·8
	17·0	9·45	80·0	20·0
70	24·2	14·1	71·6	28·4
	24·4	14·05	73·7	26·3
80	29·25	17·0	72·1	27·9
	29·3	17·0	72·4	27·6
90	27·6	16·5	67·3	32·7
	29·1	17·25	68·7	31·3
100	21·65	13·05	65·9	34·1
	21·3	13·0	63·8	36·2
120	9·5	8·15	16·6	83·4
	[illegible]75	7·8	12·2	87·8
[illegible]0	6·9	6·9	0·0	100·0

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* The irregular way in which the free chlorine escapes is probably one of the causes of the observed irregularities in the results.

TABLE III.

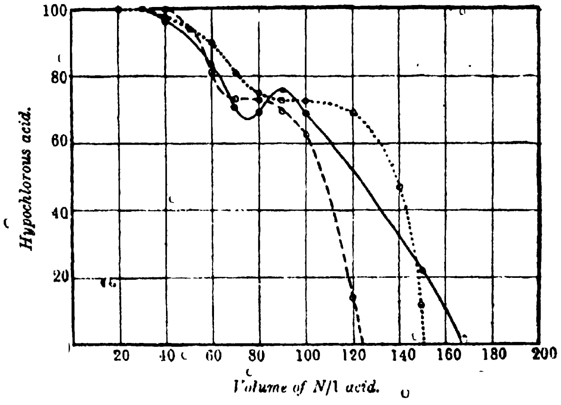
DISTILLATION WITH NITRIC ACID.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
20	0·1	0·05	100·0	0·0
30	0·1	0·05	100·0	0·0
40	4·45	2·25	98·0	2·0
50	11·8	6·1	93·4	6·6
	11·1	5·65	96·5	3·5
60	17·55	9·25	89·7	10·3
	13·5	7·05	91·5	8·5
70	20·6	11·35	81·5	18·5
	22·05	12·15	81·5	18·5
80	28·2	16·1	75·2	24·8
	28·85	16·25	77·5	22·5
90	34·5	20·75	70·6	29·4
	36·4	20·65	76·2	23·8
	29·2	16·8	73·8	26·4
100	36·85	21·4	72·2	27·8
	38·0	21·75	74·7	25·3
120	21·6	12·85	68·1	31·9
	24·4	14·1	73·0	27·0
140	13·0	8·7	49·5	50·5
	12·75	8·9	43·3	56·7
150	7·6	7·4	2·7	97·3
	8·2	7·3	12·3	87·7
	7·85	7·0	12·1	87·9
160	7·1	7·05	0·7	99·3
	6·0	6·0	0·0	100·0

It will be observed that the above results do not altogether agree with those of Kopfer: It is plain that, with an amount of acid just a little more than what is required to neutralise all the free lime, a distillate is obtained which is a moderately concentrated solution of almost pure hypochlorous acid, and in this respect there is very little difference between the three acids employed; but (and here is the principal difference between our results and those of Kopfer) long before the amount of acid is sufficient to decompose the whole of the calcium hypochlorite theoretically present in the solution (see p. 29), the proportion of hypochlorous acid has fallen to about three-quarters of its original amount, and considerable quantities of chlorine have begun to be evolved. After the point at which all the hypochlorite theoretically present is decomposed, there is, as would be expected, a rapid drop in the amount of the hypochlorous acid produced, and this drop is more rapid in the case of the hydrochloric acid than with the other acids, because immediately there is an excess of hydrochloric acid it decomposes some of the hypochlorous acid, whereas the other acids have first to liberate some hydrochloric acid from the calcium chloride present.

The curves in Fig. 1 represent the action of the three acids already described. The point where two of them are almost horizontal, and in the other an actual rise in the proportion of

Fig. 1



Continuous curve ———— H_2SO_4.
Broken ,, - - - - - HCl.
Dotted ,, ... HNO_3.

hypochlorous acid is shown, is very near where the amount of acid is just sufficient to neutralise all the free lime and to decompose all the hypochlorite present.

TABLE IV.

DISTILLATION WITH ACETIC ACID.

Volume of N-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
20	0·0	0·0	..	..
30	0·0	0·0	..	..
40	0·8	0·35	100·0	0·0
50	8·35	4·15	100·0	0·0
60	11·5	5·95	93·3	6·7
	11·5	5·9	94·9	5·1
70	15·3	8·1	88·9	11·1
	14·75	7·8	89·1	10·9
80	18·8	10·45	79·9	20·1
	18·1	10·0	81·0	19·0
90	21·1	12·35	70·8	29·2
	20·45	11·95	71·1	28·9
100	22·9	13·4	70·9	29·1
	23·9	14·0	70·7	29·3
120	25·35	14·45	75·4	24·6
	25·45	15·15	68·0	32·0
	26·0	15·1	72·2	27·8
140	25·6	15·9	61·0	39·0
	25·6	15·7	63·0	37·0
150	25·4	15·8	60·8	39·2
	25·8	15·8	63·3	36·7
170	25·0	15·7	59·2	40·8
	25·55	15·5	64·8	35·2
200	24·5	15·3	60·1	39·9
	24·5	15·5	58·1	41·9
250	22·5	15·05	49·5	50·5
	23·1	15·25	51·5	48·5
	20·8	13·55	53·5	46·5

TABLE V.

DISTILLATION WITH PHOSPHORIC ACID.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
40	3·4	1·65	100·0	0·0
50	11·35	5·85	94·0	6·0
	9·4	4·9	91·8	8·2
60	15·8	8·8	79·5	20·5
	15·55	8·55	81·9	19·1
70	21·0	12·25	71·4	28·6
	21·0	12·25	71·4	28·6
80	24·85	14·65	69·6	30·4
	26·45	15·6	69·6	30·4
90	32·7	19·1	71·2	28·8
	30·5	17·75	71·3	28·7
100	32·85	19·4	69·3	30·7
	34·05	20·2	68·6	31·4
120	33·25	20·3	63·8	36·2
	32·0	19·75	62·0	38·0
140	29·15	18·5	57·6	42·4
	30·15	19·0	58·7	41·3
150	29·4	18·75	56·8	43·2
	30·0	19·2	56·2	43·8
170	24·45	15·95	53·3	46·7
	27·2	17·2	58·1	41·9
200	24·95	16·35	52·6	47·4
250	21·6	14·2	52·1	47·9
	21·9	14·9	47·0	53·0

The action of acetic and phosphoric acids is evidently very different from that of the stronger acids. As with those, when the amount of acid is only a little more than is required to neutralise the free lime, the distillate is almost pure hypochlorous acid, although in the case of acetic acid it is considerably weaker. As the amount of acid is increased, also, free chlorine begins to be evolved long before the acid is sufficient to decompose the whole of the hypochlorite present. The diminution in the amount of hypochlorous acid proceeds much more slowly than in the case of the stronger acids, and even with so large an amount of acid as 250 c.c. the amount of hypochlorous acid in the distillate does not fall much below 50 per cent.

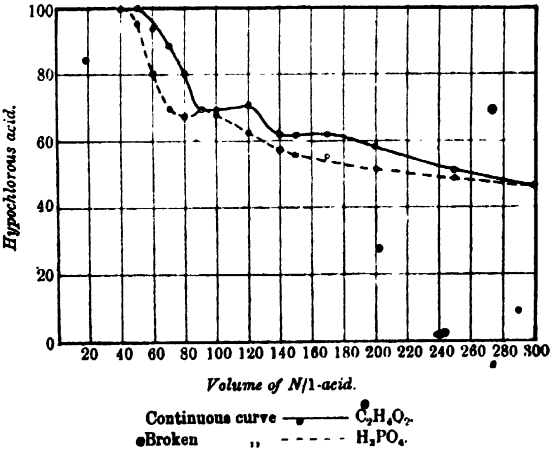
The curves in Fig. 2 represent the action of acetic and phosphoric acids. As in Fig. 1, the point where the acid is just about sufficient to neutralise the free lime and to decompose all the hypochlorite present is plainly indicated.

The Action of Boric Acid on Bleaching Powder.

A Convenient Method of Preparing a Solution of Hypochlorous Acid.

It is known that boric acid liberates hypochlorous acid from bleaching powder. Lauch (*Ber.*, 1885, 18, 2287) took advantage of this for the preparation of some additive compounds of hypochlorous acid.

FIG. 2.



Of the two constituents of bleaching powder, boric acid appears to be only able to decompose to any considerable extent one of them—the calcium hypochlorite; so that, when bleaching powder is distilled with boric acid, there is never much free chloride produced, and there is no difficulty in obtaining practically pure solutions of hypochlorous acid.

The best conditions for this purpose appear to be to distil the bleaching powder with about 30 times its weight of water and twice its weight of boric acid. So long as this proportion of water is maintained, it makes very little difference as to the amount of boric acid employed; it may even be increased to three times the weight of the bleaching powder. If, however, much less water is used, more free chlorine is produced.

If 10 grams of bleaching powder are distilled with 300 c.c. of water and any amount from 15 to 20 grams of boric acid, from 50 to 100 c.c. may be distilled off, and this will be a practically pure solution of hypochlorous acid, giving only a slight immediate turbidity with silver nitrate. This appears to us to be the simplest method of obtaining a solution of hypochlorous acid, as any ordinary variation in the proportion of acid and bleaching powder makes little difference in the result, so long as a sufficient amount of water is used, and there is not the difficulty of trying to avoid local excess of acid such as occurs when the stronger acids are employed.

The solution of hypochlorous acid so prepared is usually from 1·5 to $2N/10$, and contains from 4 to 5 grams of pure hypochlorous acid per litre.

The Action of Carbonic Acid on Bleaching Powder.

In the former paper already referred to (*loc. cit.*) it was demonstrated that, as had been stated by other observers (Wolters, *J. pr. Chem.*, 1874 [ii.], 10, 128; Lunge and Schäppi, *Dingl. Polyt. J.*, 1889, 273, 63; Dreyfus, *Bull. Soc. chim.*, 1884 [ii.], 41, 600; von Tiesenholt, *J. pr. Chem.*, 1902 [ii.], 65, 512, and 1906 [ii.], 73, 301), when carbon dioxide is passed through a solution of bleaching powder, or over the moist solid substance, no hypochlorous acid is evolved, but only free chlorine. At first sight it appears remarkable that there should be such a wide difference between the action of two such weak acids as boric and carbonic acids as is indicated by the results described above. It must be borne in mind, however, that the conditions under which the two acids were experimented with were widely different, particularly as regards temperature, and we find that under similar conditions, carbon dioxide acts practically in the same way as boric acid. If carbon dioxide is passed through a solution of bleaching powder which is kept boiling continuously, almost pure hypochlorous acid is given off. The experiment succeeds best if the carbon dioxide is bubbled fairly rapidly through the mixture of bleaching powder and water (in the same proportion as used in all the other experiments, namely, 10 grams of bleaching powder to 300 c.c. of water) from the beginning, whilst the liquid is being heated, and then the distillate collected as soon as the liquid boils vigorously. The yield of hypochlorous acid is not nearly so good if the liquid is heated first, and the carbon dioxide led in as soon as it boils. Doubtless the reason for this difference is that, when the carbon dioxide is bubbling through whilst the liquid is being heated, it is gradually removing the free lime, so that it is free to act on the calcium hypochlorite by the time the liquid is boiling.

The effect of passing carbon dioxide through a mixture of bleaching powder and water at different temperatures was tried, with the results given in Table VI.

In each experiment the mixture of 10 grams of bleaching powder and 300 c.c. of water was heated in a flask to the desired temperature. The carbon dioxide was freed from hydrochloric acid by passing it over wet glass wool. It was not passed through from the commencement, but only when the desired temperature was reached. The resulting gases were passed through 25 c.c. of $N/10$-arsenite, and the proportion of hypochlorous acid and chlorine determined in the usual way.

TABLE VI.

Temperature of mixture.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
Deg.				
30	8·75	8·3	5·3	94·7
40	10·4	9·0	15·5	84·5
50	10·2	8·75	16·6	83·4
60	8·95	7·4	20·9	79·1
70	10·25	7·35	39·4	60·6
80	11·45	8·05	42·2	57·8
90	10·6	6·7	58·2	41·8
100	10·3	5·4	90·7	9·3

As will be seen from the table, hypochlorous acid (mixed with a large proportion of free chlorine) begins to come off as soon as the liquid becomes warm, and the proportion steadily increases as the temperature rises, until when the liquid is at 100° almost pure hypochlorous acid is evolved. (In the experiment at 100° the liquid was kept as nearly as possible at that temperature. Not being pure water it did not absolutely boil. As pointed out above, if the liquid is kept actively boiling all the time the carbon dioxide is passing through, practically pure hypochlorous acid is evolved.)

We venture to submit that this remarkable difference in the action of carbonic acid at different temperatures affords strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder in the cold is the same as that of other acids, the carbonic acid decomposing both the calcium chloride and the hypochlorite, and the resulting hydrochloric and hypochlorous acids decomposing each other, with the liberation of chlorine. The solubility of carbon dioxide in water diminishes as the temperature rises, and at the boiling point of water it is practically nil, so that at that temperature the amount of true carbonic acid (H_2CO_3) present must be almost infinitesimal. Consequently, at the higher temperature it, like boric acid, can only decompose the calcium hypochlorite in the bleaching powder, with the result that pure hypochlorous acid is evolved. Further (and this, of course, is of some importance), whilst the liquid is actually boiling, the hypochlorous acid is removed from it practically as fast as it is produced. The results of our experiments at different temperatures, as expressed in Table VI., indicate the gradually diminishing amount of true carbonic acid which can exist in the water as the temperature rises, and the solubility of the carbon dioxide diminishes.

The removal of the hypochlorous acid from the solution as fast as it is produced is also an important factor in the action of boric acid on bleaching powder. As described above, when bleaching powder solution is boiled with boric acid, pure hypochlorous acid is driven off, but the action is very different at the ordinary temperature.

In the following experiments 3 grams of bleaching powder were rubbed with 100 c.c. of water, and 6 grams of boric acid added. Through this mixture air, free from carbon dioxide, was bubbled, and the issuing gases were passed through $N/10$-arsenite, with the following results:—

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1	5·0	3·76	33	67
2	6·35	4·67	36	64

The experiments took about 24 hours to produce the observed amount of oxidation in the arsenite. This means that the action is very slow as compared with the action of carbon dioxide at the ordinary temperature. This, together with the fact that not pure chlorine, but a mixture of chlorine and hypochlorous acid is evolved, leads us to the conclusion that boric acid at the ordinary temperature does not act on bleaching powder in the same way as carbonic acid and other acids. The slow evolution of chlorine we attribute to the fact that the boric acid simply unites with the free lime, and so enables the reverse action to proceed, as described in the former paper (*loc. cit.*, p. 15). The hypochlorous acid which accompanies the chlorine is doubtless due to the action of the boric acid on the calcium hypochlorite in the solution. (It must be borne in mind that, in all experiments where chlorine and hypochlorous acid are swept out by passing air through a liquid, the chlorine, being much less soluble in water, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the numbers indicate.)

The results of the above two experiments are somewhat similar to those in Table VIII. in the former paper (p. 18), which were obtained by passing air, free from carbon dioxide, through a solution of bleaching powder which had been first exposed to air in order to remove the free lime. The addition of boric acid, even in considerable quantity, is simply equivalent to exposing the bleaching powder solution to air for some time; there is apparently no action of the boric acid on the calcium chloride in the solution.

It is hardly necessary to point out that if any other acid be added to bleaching powder solution in quantity just sufficient to unite with the free lime, the effect of afterwards passing air free from carbon dioxide through the solution will be similar to what is described above. Experiments were made with hydrochloric and nitric acid. With the former the air free from carbon dioxide swept out a mixture of 85 per cent of chlorine and 15 per cent of hypochlorous acid, and with the latter 75 per cent of chlorine and 25 per cent of hypochlorous acid. One would expect the proportion of chlorine to be greater with hydrochloric acid than with nitric, because if in adding the acid to the bleaching powder solution there is at any time a local excess of acid, the former is more likely to produce free chlorine than the latter.

Summary.

(1) When bleaching powder, mixed with 30 times its weight of water, is distilled with sulphuric, hydrochloric, or nitric acid in quantity slightly greater than is required to neutralise the free lime present, hypochlorous acid mixed with a small quantity of free chlorine is evolved. When the acid is in sufficient quantity to neutralise all the free lime and to decompose the whole of the hypochlorite theoretically present, the proportion of free chlorine is considerably greater. When the amount of acid is further increased the hypochlorous acid produced rapidly diminishes, and very soon nothing but chlorine is evolved. There is not a great difference in the action of the three acids named.

(2) Acetic and phosphoric acids behave much alike, but they differ considerably, as would be anticipated, from the three acids above mentioned. Even with comparatively large amounts of these acids the proportion of hypochlorous acid evolved does not fall much below 50 per cent.

(3) When bleaching powder is distilled with boric acid and a sufficient amount of water, almost pure hypochlorous acid is produced, and there is very little difference in the result if the boric acid used is as much as three times the weight of the bleaching powder. This is recommended as a convenient method of preparing a solution of hypochlorous acid.

(4) When carbon dioxide is bubbled through a mixture of bleaching powder and water at different temperatures, whilst at the ordinary temperature nothing but chlorine is evolved, as soon as the liquid becomes warm hypochlorous acid begins to come off. The proportion of hypochlorous acid increases as the temperature rises, and when the liquid boils it is practically pure, hardly any free chlorine being evolved. It is suggested that this is strong

evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder at the ordinary temperature is like that of other acids.

(5) When boric acid is added to a solution of bleaching powder, and air free from carbon dioxide is passed through at the ordinary temperature, a mixture of chlorine and hypochlorous acid is swept out, containing a considerable excess of the former. The boric acid simply unites with the free lime, and this allows the reverse action to proceed, free chlorine being produced. If any other acid is added to a solution of bleaching powder in quantity just sufficient to neutralise the free lime, the passing of air free from carbon dioxide through the solution gives a similar result.

IV.

THE ACTION OF BLEACHING AGENTS ON THE COLOURING MATTER OF LINEN.

(From the *Journal of the Society of Dyers and Colourists*, 1912.)

In a paper recently published (*Journ. Chem. Soc.*, 1912, p. 222), S. H. Higgins describes an experiment in which he compared the bleaching action of chlorine water and a solution of bleaching powder of the same strength, as far as oxidising power was concerned, on similar samples of boiled unbleached linen, immersed for a considerable time in the solutions. He found that the linen was bleached very much more rapidly in the latter solution than in the former. Similarly, when he produced the solution of chlorine water by adding an excess of hydrochloric acid to a solution of bleaching powder, this also showed the same comparatively feeble bleaching action on the unbleached linen. He also states that "boiled cotton cloth, on saturating with bleaching powder solution and with chlorine water, was found to show a similar distinction."

I have repeated the experiments as described by Higgins, and I find that, as he says, a solution of bleaching powder bleaches linen very much more rapidly than chlorine water of the same strength does. But with cotton, if the experiment is performed in exactly the same way, the result is very different, the chlorine water acting upon it much more rapidly than the solution of bleaching powder. It would be inferred, from Higgins' description, that he had performed the experiments in the same way, but possibly "saturating with bleaching powder solution and with chlorine water" may mean some other method.

From these experiments Higgins draws the remarkable conclusion that chlorine is a much less active bleaching agent than a solution of a hypochlorite, and he concludes that the "small bleaching power of chlorine water is probably due to the presence of some hypochlorous acid in the solution." He attributes also the bleaching action of a solution of a hypochlorite mainly to the free hypochlorous acid which it may contain.

I have latterly made a considerable number of experiments on the bleaching action of chlorine, hypochlorous acid, and various solutions of hypochlorites on different colouring matters, such as turkey red, indigo, and the colouring matter of unbleached cotton. Some time ago I expressed the opinion that, contrary to what is generally believed, chlorine is usually more active as a bleaching agent than hypochlorous acid, and I may say that I am not yet inclined to alter that opinion. Consequently I was greatly surprised when I read the account of Higgins' comparative experiment with unbleached linen. The fact that chlorine there behaves so entirely differently from the way I had always found it to act induced me to try some further experiments. These experiments, I may say at once, have led me to the conclusion that the colouring matter of unbleached linen, whatever it is, is quite abnormal in its behaviour with bleaching agents, and entirely different from every other kind of colouring matter that I have experimented with. I do not know whether such an essential difference has ever been suspected before, but there appears to be no doubt of the fact.

Not only has free chlorine practically no effect on this colouring matter, but it is equally unaffected by a solution of pure hypochlorous acid. A piece of unbleached linen immersed in the latter remains brown practically as long as it does in chlorine water of the same oxidising strength. But if a small quantity of any alkali be added to the solutions, they both bleach the linen just as Higgins found the bleaching powder solution to do. Apparently what is required in order to bleach linen is a *hypochlorite*, and not either free chlorine or free hypochlorous acid; or if the latter do act it is in conjunction with the hypochlorite, which must be present.

I have carefully investigated some of the conditions under which this bleaching action takes place, and have obtained results which, in some respects, are somewhat anomalous. Thus, if it is the hypochlorite only which bleaches, it would be expected that the bleaching action would take place best when the amount of hypochlorite present was greatest, and the amount of free chlorine or hypochlorous acid least. But this is not quite the case, as the following experiments show. I used a solution of chlorine in water of such a strength that 10 c.c. required 12 c.c. of $N/10$ thiosulphate, after addition of potassium iodide, so that the chlorine water was a little stronger than decinormal and contained 4·26 grams of chlorine per litre. Eight separate portions, each of 50 c.c., of this solution were taken, and to these were added different quantities of a solution of $N/1$ sodium hydrate. Numbering the samples one to eight, to the first was added 1 c.c. of the sodium hydrate solution, to the second 2 c.c., and so on, so that in each the number of c.c. of the sodium hydrate solution added corresponded to the number of the sample.

Representing the action of the chlorine on the sodium hydrate by the following equation :

$$2NaOH + Cl_2 \rightleftharpoons NaCl + NaOCl + H_2O,$$

50 c.c. of the chlorine water would require 6 c.c. of the sodium hydrate to give the equivalent amounts represented by the equation. This was the amount added to sample No. 6. But, as the action represented above is a reversible one, this solution would still contain some free chlorine, so that the greatest amount of hypochlorite and the smallest amount of free chlorine would be contained in samples 7 and 8. Into each of the solutions similar pieces of boiled unbleached linen were placed, and in about half-an-hour it was plain that the bleaching was proceeding most rapidly in No. 4. No. 5 was almost as white, but in each direction from these two the bleaching action was slower and slower. Now samples Nos. 4 and 5 contained, in addition to sodium hypochlorite, a considerable amount of free chlorine, so that the rate of bleaching evidently does not entirely depend on the amount of hypochlorite present.

I have shown in previous papers (see pp. 19, 20) that the action of chlorine on alkalis, being a reversible action, is reversed by the addition of chlorides to the solution, especially if very little free alkali is present, producing free chlorine, so that, in the case of colouring matters other than that in unbleached linen, this addition of chlorides considerably accelerates the bleaching action. It is interesting, therefore, to consider, from the point of view of the reversibility of the action referred to, what would be the probable effect of the addition of chlorides in the bleaching of linen. Clearly it will not be the same as in the bleaching of other colouring matters.

Take, for example, the sample No. 4 in the experiments referred to above. This contains sodium hypochlorite with a certain amount of free chlorine. The addition of a chloride—common salt, for example—to this will partly reverse the action, diminishing the amount of hypochlorite present, and increasing the amount of free chlorine—making it, in fact, more like No. 3. Thus the addition of salt in this case ought to diminish the bleaching action. This is exactly what it does. Fresh mixtures were made of chlorine water and sodium hydrate similar to No. 4. To one a considerable quantity of common salt was added, and similar pieces of unbleached linen were immersed in both solutions. In half-an-hour to an hour the linen in the solution to which the salt had been added was quite distinctly less bleached than the other. On the other hand, what ought to be the effect of adding a chloride to the mixtures, say, Nos. 7 and 8? Clearly the addition of the chloride would again diminish the amount of hypochlorite, and produce a certain amount of free chlorine, making the solution, in fact, more like those lower down in the series. This ought to stimulate its bleaching action, and again this is exactly what it does. Mixtures were prepared similar to No. 7. A considerable quantity of common salt was added to one, with the result that this solution bleached the linen distinctly more rapidly than the other.

Seeing, then, that the addition of a chloride to the solution sometimes stimulates and sometimes retards its bleaching action on linen, it naturally follows that, under some conditions, it will have little or no effect at all, and I have found that adding common salt to the solution has generally much less effect on the bleaching of linen than on the bleaching of other colouring matters I have experimented with.

A series of experiments similar to those above described were tried with a solution of hypochlorous acid, using different amounts of sodium hydrate, in order to find, as in the experiments with the chlorine water, the point at which the bleaching appeared to be most rapid. The solution of hypochlorous acid was almost of the same oxidising strength as the chlorine water used in the former experiments. But, as hypochlorous acid has an oxidising power twice as great as its neutralising power, only half the quantities of sodium hydrate were used, as compared with the solution of chlorine. Again the quantities of alkali were so regulated that No. 6 in the series of eight samples was the one to which was added the amount of sodium hydrate which just satisfied the equation :

$$HOCl + NaOH \rightleftharpoons NaOCl + H_2O.$$

There is no doubt that a solution of sodium hypochlorite is to some extent hydrolysed, so that the solution No. 6 would certainly contain some free hypochlorous acid. When the bleaching power of these solutions was tested by putting in the pieces of boiled linen, the result was found to be very similar to the one with chlorine water—the bleaching proceeded most rapidly in Nos. 3 and 4, both of which must have contained, in addition to sodium hypochlorite, a considerable amount of free hypochlorous acid.

I am quite unfamiliar with the processes used in the bleaching of linen as it is usually carried on, but the results of the experiments I have described above are well worthy of the attention of those engaged in that industry. It is plain that, as I have already stated, the colouring matter of unbleached linen is quite abnormal in its behaviour to bleaching agents, and it appears to me that methods and processes which are perfectly suitable for the bleaching of cotton will not always be the best for the bleaching of linen.

It would be interesting to know whether there exist any other natural colouring matters which act in the same way with regard to bleaching agents as the colouring matter of linen. Further investigation may possibly show that linen does not stand alone in this respect.

V.

THE ACTION OF BLEACHING AGENTS ON VARIOUS NATURAL COLOURING MATTERS.

(From the *Journal of the Society of Dyers and Colourists*, 1914).

In a paper published in this Journal in 1912 (see p. 44), entitled "The Action of Bleaching Agents on the Colouring Matter of Linen," attention was drawn to the fact that the colouring matter of unbleached linen was not completely bleached either by free chlorine or by hypochlorous acid, but that a hypochlorite must be present if the linen is to be successfully bleached. Experiments were described in which different amounts of alkali were added to equal quantities of chlorine water, and pieces of boiled unbleached linen placed in them. It was found that bleaching proceeded most rapidly, and was most complete, when the amount of alkali added to the chlorine water was not quite sufficient to complete the equation :—

$$Cl_2 + 2NaOH \rightleftharpoons NaCl + NaOCl + H_2O,$$

so that the solution contained not only sodium hypochlorite, but also some free chlorine. Similar results were obtained with a solution of hypochlorous acid ; this also bleached linen most rapidly and completely when it was nearly, but not quite, neutralised by alkali according to the equation :

$$HOCl + NaOH \rightleftharpoons NaOCl + H_2O.$$

This solution contained sodium hypochlorite with some free hypochlorous acid*

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* This peculiarity of linen with respect to the action of chlorine upon it was first pointed out by S. H. Higgins (*Journ. Chem. Soc.*, 1912, p. 222). But he failed to perceive that it was a peculiarity, and he came to the remarkable conclusion that chlorine, notwithstanding its well-known bleaching properties, is generally only a very feeble bleaching agent, except when in what he calls a "nascent" state, the exact meaning of which it is difficult to gather. He attributed, and apparently continues to attribute, all bleaching properties of chlorine and bleaching powder solutions to free hypochlorous acid. There

Until this apparently quite abnormal behaviour of the colouring matter of linen to bleaching agents was pointed out, it was customary to take the results of bleaching experiments with such colouring matters as turkey red and indigo as reliable guides to bleaching action in general. But it is now quite plain that in estimating bleaching actions the nature of the colouring matter must be taken into account. Thus, in the case of the colouring matters just mentioned (turkey red and indigo), they are both rapidly bleached by free chlorine and by hypochlorous acid, and hardly at all, or at any rate very slowly, by a solution of a hypochlorite which contains little if any free chlorine. In the experiments referred to above, where increasing amounts of alkali were added to chlorine and to hypochlorous acid, the bleaching action of the solutions so obtained upon turkey red and indigo depends absolutely upon the amount of free chlorine or hypochlorous acid present, so that the bleaching action is greatest before the addition of any alkali, and becomes less and less as more alkali in proportion to the chlorine or hypochlorous acid is added.

With regard to the action of chlorine and of hypochlorous acid upon the colouring matter of linen, it is a mistake to say that they have no action at all upon it. Experiments show that when boiled unbleached linen is placed in a solution of chlorine or of hypochlorous acid they do act upon it to a certain point; but beyond that point the remaining colouring matter is discharged very slowly indeed. There is practically no difference between the two bleaching agents with regard to the rate of, or the extent of this bleaching action. The subsequent addition of a small amount of alkali (which must be as nearly as possible the right amount) to either of the solutions causes the bleaching action on the remainder of the colouring matter to proceed until the bleaching is more or less complete.

These experiments appear to show that there are two kinds of colouring matter in unbleached linen. While these two colouring

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does not appear to be any justification for such a conclusion. I pointed ou in the paper already referred to that hypochlorous acid behaves with th colouring matter of linen almost exactly as chlorine does; it does not bleac it completely until it is partly neutralised. I have tried a great man experiments on the comparative bleaching activities of chlorine and hypochlorous acid, the details of which I hope to publish shortly, and I hav come to the conclusion that chlorine is definitely and nearly always a mor active bleaching agent than hypochlorous acid.

matters may in most respects be like each other, they are different in their behaviour to chlorine and hypochlorous acid. One of the two is almost unbleached by those agents, but is bleached by an alkaline hypochlorite. The other is bleached rapidly by chlorine or hypochlorous acid, but very slowly by a hypochlorite.

The action of chlorine and hypochlorous acid upon the colouring matter of cotton is deceptive. (Distinction has usually to be made between American and Egyptian cotton. The latter, as is well known, is much darker in colour than the former; that is, it contains much more colouring matter. Apart from the difference in amount, there does not appear to be any essential difference in the nature of the colouring matter in the two kinds of cotton).

The moment unbleached cotton is placed in chlorine water or in a solution of hypochlorous acid, the bleaching begins, and proceeds with much greater rapidity than is the case with linen. In a comparatively short time the cotton appears to be white. Until recently the author was under the impression (as most people are still) that chlorine bleaches cotton completely. But this is wrong. There is a small residual amount of colouring matter in cotton which is not destroyed either by chlorine or by hypochlorous acid, even by prolonged contact. It is bleached, however, by a solution of a hypochlorite. So that cotton, like linen, apparently contains two different kinds of colouring matter with similar characteristics to those in linen. The great difference between cotton and linen is in the proportions of the two different kinds of colouring matter. Linen contains a comparatively large proportion of that kind which is not bleached by chlorine or by hypochlorous acid, while cotton contains a much smaller proportion.*

The natural colouring matter in jute also appears to be of the same nature. It is very difficult to bleach completely, but it shows the same characteristics as linen. The bleaching action of chlorine and hypochlorous acid on jute proceeds to a certain point and then stops; but when an amount of alkali not quite sufficient to complete the action on the chlorine or hypochlorous acid is added, the bleaching action at once proceeds much further.

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*In 1871 E. Schunck (*Manchester Lit. and Phil. Soc. Memoirs*, pp. 95-128) pointed out that two distinct kinds of colouring matter were dissolved out from cotton by boiling it with a solution of soda-ash. He referred to the action of bleaching agents on one of them, but not on the other.

It is perfectly plain, then, that the bleaching action of chlorine, etc., upon such natural colouring matters as those described above is very different from their action on indigo and turkey-red, for instance; hence it is quite misleading to draw definite inferences as to rapidity, etc., of bleaching action from either of the two classes of colouring matters. In the case of indigo and turkey red, as pointed out above, the rapidity of bleaching depends absolutely upon the amount of free chlorine or hypochlorous acid present, and anything which would increase that amount would stimulate the bleaching. But this is evidently not the case with the other colouring matters.

There is one point, however, in which the two classes of colouring matters are almost alike, and that is in the great retarding influence which alkalis, when in excess, have on the bleaching action. In former papers this has been pointed out again and again, and in all bleaching operations it must be borne in mind. The retarding influence of an excess of alkali is even greater with indigo and turkey red than with the natural colouring matters of linen and cotton, but even with the latter it is very considerable.

Apparently, then, the best bleaching solution for both linen and cotton is one which contains little or no free alkali, but rather a slight excess of chlorine or hypochlorous acid. In order to illustrate this, the following experiments (out of many which have been tried) may be described. Six separate portions, each 50 c.c., of chlorine water were taken, and to five of these were added different amounts of a solution of *N*/1 sodium hydrate. The chlorine water was approximately decinormal. Numbering the samples from 1 to 6, sample No. 1 consisted of chlorine water alone; to No. 2 were added 2 c.c. of the sodium hydrate solution; to No. 3 were added 3 c.c., and so on, so that the last had 6 c.c. of the sodium hydrate added to it. The chlorine water was of such a strength that No. 5 contained the exact amount of sodium hydrate required by the equation :—

$$2NaOH + Cl_2 \rightleftharpoons NaCl + NaOCl + H_2O.$$

As the action represented thus is a reversible one, this solution would still contain some free chlorine, so that the greatest amount of hypochlorite and the smallest amount of chlorine would be contained in No. 6.

Into each of these solutions samples of boiled unbleached linen, Egyptian cotton and American cotton were placed. In one experiment, in which the time of bleaching was two hours, Nos. 3 and 4 were by far the best in the case of the pieces of linen, and also quite plainly the best in the case of both kinds of cotton. In another precisely similar experiment, only continued for six hours, in the case of linen No. 4 was distinctly the best, while with the two kinds of cotton it was difficult to choose between Nos. 4 and 5. In all the cases, however, No. 1 (free chlorine) and No. 6 (containing a considerable amount of free alkali) were distinctly the worst. (Samples showing the results of these experiments were exhibited).

Exactly similar experiments with hypochlorous acid gave very similar results. In this case again No. 1 contained free hypochlorous acid, which was of such a strength that No. 4 contained exactly sufficient sodium hydrate to unite with it. Experiments lasting, again, two and six hours respectively were tried. In the case of the linen No. 2 was distinctly the best in both experiments, while with both kinds of cotton it was difficult to discriminate between Nos. 2, 3, and 4. In all cases, again, Nos. 1 and 6 were the worst. (Specimens showing the results of these experiments were exhibited).

The results of these experiments show pretty clearly what are the conditions to aim at in bleaching with a solution of bleaching powder. The latter always contains a considerable amount of free lime, some of which, of course, dissolves up when the solution of bleaching powder is prepared, and this free lime must considerably retard the bleaching action. If the free lime can be removed, then conditions more or less similar to those in the experiments described above will be realised. Of course, the removal of free lime is perfectly simple. One method would be to add more chlorine to the bleaching powder solution, and this method acts perfectly well on a small scale, but although chlorine is a more available substance at the present time than it formerly was, that is hardly a practicable method. Another method would be to neutralise the free lime by the addition of an acid—say hydrochloric acid. Of course, the addition of various acids to solutions of bleaching powder has from time to time been recommended, but if such a process is practised at all it is certainly not universal.

To obtain good results by the addition of an acid to bleaching powder solution, the thing would have to be done very carefully indeed. The addition of too large a quantity of acid would be probably worse than adding none, and it may easily have occurred that, where experiments have been made in this direction, the results will have been too irregular to inspire any confidence in the method.

A number of experiments on the addition of acid in varying amounts to solutions of bleaching powder have been made, in order, if possible, to realise the conditions which I have pointed out would be best. For some time the results were very irregular and unsatisfactory, simply because the experimenter had failed to take into account what ought always to be borne in mind when using solutions of bleaching powder. The fact is that the amount of free lime which a solution of bleaching powder in water will contain (and hence the amount of acid required to neutralise it) depends not on the bleaching strength of the solution, but upon the way the solution has been made. Lime is very much less soluble in water than the other constituents of bleaching powder, so that if different amounts of bleaching powder are stirred up with equal amounts of water, the absolute amount of lime dissolved in each case will be approximately the same. In all cases there will be practically a saturated solution of lime, whereas the quantity of the more soluble bleaching constituents will be much greater in some cases than in others. The proportion of lime to the bleaching constituents will be much smaller in the stronger solutions than in the more dilute.

Thus, bleaching powder ground up with 100 times its weight of water produces a solution from 1 deg. to 1½ deg. Tw., and approximately decinormal in its oxidising strength. The same weight of bleaching powder with ten times its weight of water (1 lb. to a gallon) gives a solution about 10 deg. Tw., and approximately normal. Equal volumes of both (clear) solutions would contain approximately the same amount of free lime. If the stronger solution were diluted with nine times its bulk of water it would be of exactly the same oxidising strength as the dilute solution made directly, but it would only contain one-tenth as much free lime, which would only require one-tenth as much acid to neutralise it. Such a dilute solution, prepared by diluting a much stronger solution, is by itself more active in bleaching than the one made directly. In the case of two pieces of turkey red calico, which had been immersed for 20 hours in solutions exactly such as those just described, the one which had been in the diluted down solution was almost completely bleached, while the othe was hardly touched. A considerable difference was also observed with two pieces of linen which had been immersed for some time in the same solutions; and yet the two solutions were both solutions of bleaching powder alone, and both of exactly the same bleaching strength.*

Taking all this into account, and especially if we know the amount of free lime present in the solution, there is no difficulty in preparing bleaching solutions which, judging from the results of my experiments, ought to be most suitable for bleaching, either in the case of linen or cotton.

A strong solution of bleaching powder was made, standing at 10 deg. to 11 deg. Tw. It was approximately a normal solution. The clear solution was diluted with five times its volume of water, which reduced it to 1·5 deg. to 1·7 deg Tw., and the oxidising strength to $N/10 \times 1·5$. Seven separate portions (50 c.c.) of this solution were taken, numbered 0 to 6, and different amounts of $N/10$ hydrochloric acid added to six of them (1 c.c. of acid to No. 1, 2 c.c. to No. 2, and so on, No. 0 having no acid added) The amount of free lime originally present in the strong solution was determined, and it was such that it would be almost exactly neutralised in No. 3 solution. Pieces of linen, Egyptian cotton, and American cotton were placed in each solution and left there for three hours.

In the case of the linen, No. 3 was distinctly the best bleached, and the result was the same with the Egyptian cotton. With the American cotton No. 4 was the best, and No. 5 was almost as good. It is plain, however, from this experiment that if this method of adding acid to the bleaching solution is adopted it will have to be done with care and discretion. As a guide to anyone who may wish to try this on a larger scale, it may be pointed out that the amount of acid to be added works out to half a pint of ordinary commercial hydrochloric acid to 100 gallons of the diluted bleaching liquor. This would be the amount for linen or Egyptian cotton; for American cotton about one-third more would be required, as in this case there appears to be a rather wider margin as to the amount of acid which may safely be added.

No experiments have been made with acids other than hydrochloric acid. There appears to be no reason at all why one acid should be better than another, and ordinary sulphuric acid might probably be used instead of hydrochloric acid. In that case the quantity required for 100 gallons of the bleaching liquor would be 5 oz. to 6 oz. (by weight) or 3 oz. to $3\frac{1}{2}$ oz. by measure of strong oil of vitriol. Whichever acid is used, it should be diluted with water first, and the bleaching liquor should be well stirred while it is being added.

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* I have found, since writing the above, that what I have stated with regard to the making of bleaching solutions in different ways and their different bleaching actions when so made, was pointed out by W. Kind in 1910 (*Deutsche Farberzeitung*).

Of course the results just described were obtained with one particular sample of bleaching powder, but while there is no doubt that bleaching powder varies somewhat in composition, it is pretty certain that a solution of the strength described made from any specimen of bleaching powder which was not really too old would have pretty nearly the same composition as the one used. It would in all probability contain the same proportion of free lime, and that is the most important point.

These experiments were carried out on a very small scale, and it does not always follow that operations which are successful in the laboratory are equally successful in the works. But investigation on a larger scale, carried out on the lines suggested in this paper, would in all probability have valuable results.

NOTE.—Since the above paper was read, at the suggestion of Dr. Knecht further experiments have been tried in order to ascertain whether the alkali which, when added to chlorine water or hypochlorous acid in exactly the right amount increases the bleaching action, acts itself upon some of the colouring matter which the chlorine or hypochlorous acid were unable to bleach.

Some pieces of linen, Egyptian cotton, and American cotton were immersed in chlorine water for 18 hours. They were then cut in two, and portions of each washed out and immersed in a very dilute solution of sodium hydrate. The other portions were immersed in an ordinary dilute solution of bleaching powder, in which solution the bleaching proceeded considerably further. In the dilute alkali, however, there was no further bleaching ; if anything, the pieces became darker. Plainly, the alkali does not act itself upon the colouring matter, but only the hypochlorite which it produces when added to the chlorine water or hypochlorous acid. Also, if cotton is boiled with water merely, instead of with an alkaline solution, the subsequent action of chlorine, and of chlorine plus alkali, upon it is practically the same.

VI.

A RAPID METHOD OF DETERMINING CHLORIC ACID AND CHLORATES.

(From the *Journal of the Society of Dyers and Colourists*, 1916.)

If some dilute hydrochloric acid is added to a solution of, say, potassium chlorate to which some potassium iodide has been added, there is no liberation of iodine for some time. But after a while the solution turns yellow and ultimately brown, owing to the gradual liberation of iodine. The following equation represents the change which ultimately occurs :—

$$KClO_3 + 6HCl + 6KI = 7KCl + 3H_2O + 6I.$$

The rate at which this decomposition proceeds depends upon the amount of hydrochloric acid in the solution, and if that amount is quite small the reaction will not proceed to completion. The change is accelerated by a rise of temperature, and one well-known method of determining chloric acid and chlorates is by heating a mixture such as the above, containing a moderate amount of hydrochloric acid, in a sealed bottle, to the temperature of boiling water for a considerable time, and then determining the amount of iodine liberated by titrating with thiosulphate in the usual way. But if a large excess of hydrochloric acid is added to such a mixture of chlorate and iodide, the reaction finishes at once or within half a minute, and the chlorate is completely decomposed, with the liberation of a corresponding amount of iodine. This fact is the basis of the method proposed for the rapid determination of chloric acid and chlorates. In carrying out the process there is added to the solution in which the chloric acid or chlorate is to be determined, and to which a sufficient amount of potassium iodide has been added, from one and a half times to twice its own bulk of concentrated hydrochloric acid. The hydrochloric acid which one usually obtains is so strong that the liquid to which it is added becomes perceptibly warmer, and doubtless this rise of temperature accelerates the decomposition of the chloric acid. It has been stated that reliable titrations with thiosulphate cannot be performed in solutions containing a large amount of free acid. But no difficulty is experienced provided that the titration is performed as rapidly as possible, and the solution is diluted with about half its volume of water before titrating.

In order to keep down as far as possible the total volume of the liquid, it is best to use the solution containing the chlorate to be determined of such a concentration that not more than 10, or at the most 20 c.c. of it need be used for each experiment. For the same reason also the potassium iodide required is best added in the form of a few crystals of the solid, rather than in solution.

This method has been thoroughly tested with solutions of pure chlorates of known strength, and with uniformly accurate results. It has also been used in the course of some investigations on the decomposition of solutions of hypochlorous acid, which contained both hypochlorous and chloric acids. In those experiments the amount of available material was usually small, and it was found possible to economise this by determining both hypochlorous acid and chloric acid in the same portion of the solution. The hypochlorous acid is first determined by adding potassium iodide and a few drops of dilute hydrochloric acid and titrating with thiosulphate in the usual way. Then to the same liquid is added about twice its volume of concentrated hydrochloric acid, when there is a further liberation of iodine due to the decomposition of the chloric acid, and this is further titrated for the amount of chloric acid present.

Determination of Calcium Chlorate in Bleaching Powder.

This method may be used for the determination of the amount of calcium chlorate in bleaching powder. In this case also the hypochlorite (" available chlorine ") and chlorate may both be determined in the same portion of the solution. But, as pointed out above, it is very desirable to keep down as far as possible the total bulk of the liquid to which the large excess of hydrochloric acid has to be added. A considerable volume of thiosulphate is usually required in determining the available chlorine, and when afterwards strong hydrochloric acid has to be added to the extent of twice the volume of the solution, and this again to be diluted somewhat before titration, the liquid becomes inconveniently bulky. Furthermore, it has been found in numerous experiments that when done in this way the results are not so uniform as is desirable, so that it is preferable to make separate determinations of available chlorine and of calcium chlorate.

The process recommended is as follows: The bleaching powder is ground up with water so as to make a solution containing 20 grammes per litre; 10 c.c. of this are used for determining the available chlorine in the usual way by adding potassium iodide and a little acetic acid and titrating with decinormal thiosulphate. Then 10 c.c. more are taken for the determination of available chlorine and chlorate together. A few crystals of potassium iodide are added, and when these are quite dissolved 20 c.c. of concentrated hydrochloric acid are added, then a little water, and the solution titrated as before. The difference between the amounts of thiosulphate used in the two experiments represents the amount of chlorate present. If the number of c.c. in this difference be represented by N, then N × 0·864 gives the percentage of calcium chlorate in the bleaching powder.

It is necessary to point out that the amount of calcium chlorate usually present in bleaching powder is very small, so that the difference between the volume of thiosulphate solution required in the two separate determinations will frequently amount to less than one cubic centimetre, and will seldom be more than two, so that the determination of the chlorate cannot be done with very great accuracy. But the same objection applies to other methods of determining chlorate in bleaching powder, unless it is possible to use much larger quantities in the determinations.

VII.

THE EFFECT OF LIGHT ON SOLUTIONS OF BLEACHING POWDER.

(From the *Journal of the Society of Dyers and Colourists*, 1917).

It is well known that bleaching powder deteriorates somewhat rapidly when kept, whether in the solid state or in solution.

In 1886 and 1888 (*J. Soc. Chem. Ind.*, V. 587 and VII. 188) J. Pattison described some experiments on the changes which solid bleaching powder undergoes when kept in casks and in bottles at the ordinary temperature, and also at temperatures of 70°F. and 80°F. He found, as would be expected, that at the latter temperature the change was more rapid than at the ordinary temperature of 60°F. Thus, while bleaching powder at 60°F. lost 17 per cent of its available chlorine in 12 months, at 80°F. the loss in the same time amounted to 47 per cent. Pattison, however, makes no mention in these experiments of the conditions as regards the admission or exclusion of daylight.

About the same time G. Lunge and L. Landolt published a somewhat comprehensive paper entitled " An Investigation into the Modes of Formation, Properties, etc., of certain Bleaching Agents (hypochlorites) " (*Journ. Soc. Dyers and Col.*, 1885, pp. 281–287), in which they described some experiments " on the changes which bleaching solutions undergo on keeping." In these experiments they used solutions not only of bleaching powder but also of the hypochlorites of magnesium, zinc and aluminium, which they prepared by the interaction of the sulphates of those metals with solutions of bleaching powder. They described three sets of experiments, in which the solutions were kept (*a*) in closed vessels in the dark, (*b*) in open vessels in the dark, and (*c*) in closed vessels in diffused daylight. They found considerable differences in the behaviour of the different hypochlorites under some of these conditions, but these differences, while of some theoretical importance, do not particularly concern us at the present time. But the experiments with bleaching powder solution were of considerable interest, and the results, as they pointed out at the time, were of great practical importance. The solutions were analysed at intervals of two or three days, and it was found that, while the solution kept in the dark in closed vessels remained almost without loss of strength for nearly a month, that which was exposed to diffused daylight began to change almost at once, and ultimately lost a considerable amount of its available chlorine. The solution kept in an open vessel in the dark naturally lost strength more rapidly than that in the closed vessel. No mention is made of the kind of open vessel used (that is, the extent to which air would have access to the solution), but there is no doubt that under these circumstances the rate of change of the solution would depend mainly upon the amount of air having access to it.

It is not quite clear, in these experiments of Lunge and Landolt, what were the exact strengths of the solutions they used (they simply state that a concentrated solution of bleaching powder was mixed with an equal bulk of water), and, while they state definitely that Series A were analysed at intervals of three days and Series B at intervals of two days, no mention of any time is made with regard to Series C (solutions exposed to diffused daylight).

The experiments described in the present paper were started before I was aware of Lunge and Landolt's experiments. As will be seen, they confirm their general conclusions in the main, but they extend over a much longer time, and I am able to add some information as to the character of the change which takes place in the solutions.

Three series of experiments were made, namely :—

A. Solutions kept in stoppered bottles in the dark

B. Solutions in stoppered bottles exposed to diffused daylight on the laboratory shelves in a room not over well lighted by windows on one side.

C. Solutions in stoppered bottles standing in a window, exposed to diffused daylight during the greater part of the day, and to direct sunlight for a few hours on sunny days.

In each series of experiments three different solutions bleaching powder were used, namely :—

No. I.—50 grammes of bleaching powder in a litre of water, equal to half a pound to a gallon of water, giving a solution about 5 deg. Tw.

No. II.—10 grammes of bleaching powder in a litre of water, equal to four-fifths of an ounce to a gallon of water, giving a solution from 1 deg. to 1½ deg. Tw.

No. III.—No. I. solution, after standing till clear, diluted to one-fifth of its strength with water, thus giving a solution practically the same strength as No. II., but which would contain much less free lime than the latter. It was assumed and, as will be seen, correctly, that the amount of free lime present would make some difference in the stability of the solution.

The series of experiments A and B were started at the beginning of July, 1916, and the last observations were made on October 8th, 1917, so that they extended over 15 months. Series C were started on July 18th of the present year (1917), and continued to October 9th—about 12 weeks.

At irregular intervals, short at first but much longer afterwards, small measured quantities of the solutions were taken, and the available chlorine determined, after adding a little potassium iodide and a few drops of dilute hydrochloric acid, by means of a decinormal solution of sodium thiosulphate. (No. I. being rather a strong solution, only 5 c.c. were taken for each determination of the available chlorine ; with Nos. II. and III. 10 c.c. were taken for each experiment).

In a paper read before this Society in 1916 (see Paper VI., p. 57), I described a method for the rapid determination of chloric acid and chlorates. I showed that if, instead of adding a small quantity of dilute acid to a solution of a hypochlorite (such as bleaching powder) to which potassium iodide has been added, a considerable volume, amounting to at least twice the volume of the liquid operated upon, of concentrated hydrochloric is used, the whole of any chlorate which may be present is completely decomposed, with the liberation of a corresponding amount of iodine. Subsequent titration with solution of thiosulphate will then give a measure of the total hypochlorite and chlorate present in the solution. By subtracting from this the amount of thiosulphate required for titration of the iodine liberated by the addition of dilute acid (due to hypochlorite alone) the amount of chlorate in the solution is found. This is a reliable method for determining the amount of chlorate in a sample of bleaching powder, and has been employed in the experiments now described as a means of ascertaining the kind of reaction which occurs in those solutions in which the calcium hypochlorite undergoes any change.

It is, of course, well known that solutions of hypochlorites change very rapidly when heated, and there does not appear to be any doubt that the change which occurs is essentially that represented by the following equations :—

$$3NaOCl = NaClO_3 + 2NaCl$$

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$$

Quite recently the mechanism of the conversion of sodium hypochlorite into chlorate at a temperature of 50 °C. has been investigated by F. Foerster and P. Dolch (*Zeitsch. Electrochem.*, 1917, 23, [illegible]145). They conclude that the change takes place in two steps : first, the conversion of hypochlorite into chlorite and chloride ($2NaOCl = NaClO_2 + 2NaCl$), the chlorite then reacting with hypochlorite to produce chlorate and chloride ($NaClO_2 + NaOCl = NaClO_3 + NaCl$). There is also some evolution of oxygen, which they attribute to the simple decomposition of hypochlorite into chloride and oxygen ($2NaOCl = O_2 + 2NaCl$).

The results of my experiments are shown in the following tables. Column 1 gives the times which elapsed between the separate observations, Column 2 the amount of thiosulphate required for titration of the iodine liberated by the addition of potassium iodide and dilute hydrochloric acid (representing the amount of hypochlorite present in the solution), and Column 3 the thiosulphate required after the addition of potassium iodide and concentrated hydrochloric acid, which represents the oxidising power of the hypochlorite and chlorate together. By subtracting the numbers in Column 2 from those in Column 3, numbers are obtained which indicate the amount of chlorate present in the solution, from which can be inferred the amount of hypochlorite changed into chlorate. These numbers are given in Column 4.

If the change which the calcium hypochlorite undergoes were entirely what one may call the normal change (the conversion into chlorate according to the equation $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$), then the total oxidising power of the solution would remain unchanged. The figures in Column 3 represent the total oxidising power of the solutions, and it will be observed that in all the experiments in which the solutions underwent any change the total oxidising power diminished to a greater or lesser extent. This was due to an actual evolution of oxygen, which always occurred.

SERIES A.

SOLUTION No. I. (50 grms. bleaching powder in a litre of water, kept in the dark).

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	Difference between 3 and 2.
..	23·85	24·9	1·05
3 days	23·7	24·9	1·2
5 ,,	23·8	24·8	1·0
10 ,,	23·6	24·7	1·1
17 ,,	23·6	24·7	1·1
3 months	22·25	23·65	1·4
6 ,,	21·65	23·25	1·4
10 ,,	20·6	22·4	1·8
11 ,,	20·4	22·2	1·8
12 ,,	20·2	22·1	1·9
15 ,,	18·6	20·7	2·1

In this solution the loss of hypochlorite amounted to 22 per cent. Of this only 20 per cent was converted into chlorate, 80 per cent being lost as free oxygen.

SOLUTION No. II. (10 grms. of bleaching powder in a litre of water, kept in the dark).

In this solution there was practically no change at all during the whole of the 15 months that it was kept. The first and the final figures only are given.

Time.	With Dilute HCl.	With Concentrated HCl.
..	9·7	10·35
15 months	9·55	10·15

SOLUTION No. III. (the clear solution No. I. diluted to one-fifth of its volume, kept in the dark).

As in Solution No. II. there was practically no change. The first and final figures only are given.

Time.	With Dilute HCl.	With Concentrated HCl.
..	9·4	9·9
15 months.	9·3	10·03

SERIES B.

SOLUTION No. I. (50 grms. bleaching powder in a litre of water, kept in diffused daylight).

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	23·5	24·5	1
2 days	23·5	24·4	0·9
5 „	23·4	24·5	1·1
10 „	22·9	24·3	1·4
17 [illegible]	22·5	24·1	1·6
3 months	17·4	23·1	5·7
6 „	16·3	23·1	6·8
10 „	1[illegible]·6	22·6	9·0
11 „	12·3	22·5	10·2
12 „	11·6	22·5	10·9
15 „	8·4	21·7	13·3

Loss of hypochlorite = 64 per cent, 82 per cent of which was converted into chlorate.

SOLUTION No. II. (10 grms. bleaching powder in a litre of water, kept in diffused daylight.)

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	9·45	9·9	0·45
2 days	9·4	9·9	0·5
5 „	9·3	9·9	0·6
10 „	9·2	9·8	0·6
17 „	8·9	9·6	0·7
3 months	6·9	9·0	2·1
6 „	6·65	8·9	2·25
10 „	6·0	8·75	2·75
11 „	5·15	8·5	3·35
12 „	4·7	8·5	3·8
15 „	3·4	8·0	4·6

Loss of hypochlorite = 64 per cent, of which 69 per cent was converted into chlorate.

SOLUTION No. III. (solution No. I. diluted to one-fifth of its volume, kept in diffused daylight).

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	9·1	9·68	0·58
5 days	8·9	9·5	0·6
12 „	8·6	9·3	0·7
3 months	5·9	9·0	3·1
6 „	5·35	8·65	3·3
10 „	4·35	8·55	4·2
11 „	3·3	8·25	4·95
12 „	2·9	8·2	5·3
15 „	1·65	7·7	6·05

Loss of hypochlorite = 82 per cent, of which 73 per cent was converted into chlorate.

SERIES C.

SOLUTION No. I. (50 grms. bleaching powder in a litre of water, exposed to diffused daylight with intermittent direct sunlight).

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	20·3	22·3	2
7 days	17·7	22·6	4·9
12 weeks	4·8	18·25	13·45

Loss of hypochlorite -- 76 per cent, of which 74 per cent was converted into chlorate.

SOLUTION No. II. (10 grms. bleaching powder in a litre of water, exposed to diffused daylight with intermittent direct sunlight.)

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	8·7	9·8	1·1
7 days	6·9	8·9	2
12 weeks	0·5	5·5	5

Loss of hypochlorite = 94 per cent, of which 48 per cent was converted into chlorate.

SOLUTION No. III. (solution No. I. diluted to one-fifth of its volume, exposed to diffused daylight with intermittent direct sunlight).

1 Time.	2 Dilute HCl.	3 Concentrated HCl.	4 Difference between 3 and 2.
..	8·2	9·05	0·85
7 days	7·0	8·6	1·6
12 weeks	0·1	5·85	5·75

Loss of hypochlorite = 99 per cent, of which 60 per cent was converted into chlorate.

Frequently bubbles of gas were observed ascending in the solutions, especially on shaking, and an excess of free oxygen could always be detected in the air at the top of the bottles when they had remained closed for any considerable time. As mentioned above (p. 63), Foerster and Dolch, in their experiments with sodium hypochlorite, found that oxygen was always evolved, and I have no reason to doubt that their explanation of this—the decomposition of some of the hypochlorite into chloride and free oxygen—is correct. There does not seem to be any great regularity in the extent to which this loss of oxygen occurs in the various solutions, but, curiously enough, it was relatively greatest in the strong solution of bleaching powder which was kept in the dark, and that solution, of all the solutions which changed at all, changed the least. But it must be borne in mind that a number of catalytic agents will cause bleaching powder to give off oxygen, and it is quite possible that small quantities of one of these may have been present in the solutions.

It will be observed that, in the solutions in Series B, where they were exposed to diffused daylight, the rate of decomposition was very irregular, the amount decomposed during one interval of three months, for example, being much greater than during the next similar period. This irregularity was due to the varying amounts of light during different periods of the year. The period of three months during which a comparatively small amount of decomposition took place was in the winter time, when for days or weeks in succession very little daylight was experienced in Manchester.

In a former paper which I read before this Society on "The Action of Bleaching Agents on various Natural Colouring Matters" (see Paper VI.), I drew attention to the different behaviour of solutions of bleaching powder of the same strength, but prepared in different ways. Bleaching powder always contains a very considerable amount of free lime, and, as this is by far the least soluble of its constituents, any given amount of water, when shaken with varying amounts of bleaching powder, while dissolving different quantities of the bleaching constituents, will always dissolve the same amount of lime (unless the quantity of bleaching powder used be very small indeed). So that a solution of bleaching powder prepared by diluting a stronger (clear) solution with water will naturally contain relatively less free lime than a solution of the same oxidising strength prepared by simply stirring up the requisite amounts of bleaching powder and water and allowing the solution to stand till clear.

The solutions numbered II. and III. in the experiments now described stand in this relationship to each other. They are both approximately of the same oxidising strength, but No. III. solution, prepared by diluting solution No. I., only contains one-fifth as much free lime as No. II. In the former paper referred to above it was pointed out that of such solutions the one containing the smaller amount of free lime bleaches considerably more rapidly than the other, and I felt confident that this same solution would also be more liable to decompose than the other. Reference to the tables showing the experiments in Series B and C will show that this was actually the case. In Series B, while Solution No. II. lost 64 per cent of its available chlorine, Solution No. III. lost 82 per cent; and in Series C, while Solution No. II. lost 94 per cent, Solution No. III. was practically completely decomposed. There is no doubt that the proportion of free lime present in a solution of bleaching powder has considerable influence on its stability, as well as on its bleaching activity.

In these experiments, the results obtained in Series A appear to me the most remarkable. I certainly never anticipated that solutions of such a recognisedly unstable substance as bleaching powder could be kept, under any circumstances, for 15 months without undergoing any decomposition at all. It would almost appear that, in the dark, dilute solutions are practically everlasting. On the other hand, why the strong solution (which, after all, was not very concentrated) should partly decompose, while the two dilute solutions remained unchanged, is difficult to understand, unless, as already suggested, the strong solution may have contained a small amount of some catalytic agent which would cause the decomposition. It is also worth noting that the presence of much or little free lime has no influence on the stability of solutions kept in the dark.

As to the practical technical importance of the results of these experiments, I can only repeat what Lunge and Landolt said with reference to the results of their experiments: " It is, therefore, of great importance in keeping bleaching solutions for use to preserve them from the action of light."

VIII.

NOTES ON HYPOCHLOROUS ACID AND CHLORINE, WITH COMPARISONS OF THEIR BLEACHING ACTION.

(From the *Journal of the Society of Dyers and Colourists*, 1922.)

The hypochlorous acid used in the following experiments was prepared by distilling bleaching powder, mixed with 30 times its weight of water, with twice its weight of boric acid, as described in a former paper (see paper No. III., p. 37). The solution of hypochlorous acid so obtained is generally about $N/10 \times 1{\cdot}5$ in oxidising power, and contains about 4 grms. of the pure acid per litre.

The solution is quite colourless. When kept, it is fairly stable in the dark, but decomposes more or less rapidly in presence of light in ways previously described by several observers. In bright sunlight it soon turns yellow, and oxygen is slowly evolved. In ordinary diffused daylight two samples lost 63 per cent and 87 per cent of their oxidising power in five and six months respectively. Another similar sample kept in the dark lost 28 per cent in five months, while still another, kept sealed up in a small flask in the dark, lost only 50 per cent in six years.

During the decomposition of hypochlorous acid, chloric acid and hydrochloric acid are always produced, together with some oxygen and some chlorine. The decomposition probably proceeds in the first instance as follows, corresponding to the well-known change of hypochlorites into chlorates and chlorides—

$$3HOCl = HClO_3 + 2HCl.$$

But as soon as any hydrochloric acid is produced in this reaction it would immediately react with some of the hypochlorous acid and liberate chlorine. This is probably what takes place in direct sunlight, when there is a manifest liberation of chlorine, which is not the case in ordinary daylight with an acid of the strength described.

Decomposition of Hypochlorous Acid in presence of Silve Nitrate.

When a solution of hypochlorous acid is mixed with one o silver nitrate, only a slight milkiness is observed at first, but this soon increases, and a curdy white precipitate of silver chloride begins to form, which continues to increase. The decomposition of the hypochlorous acid proceeds quite rapidly under these conditions. The change which takes place is that represented by the equation given above (into chloric and hydrochloric acids), but the immediate removal of the latter by the silver solution greatly stimulates the decomposition. The change is almost complete in a few hours, although a little hypochlorous acid usually remains at the end of 24 hours. The greatly increased rapidity of decomposition of hypochlorous acid by the immediate removal of the hydrochloric acid formed suggests that the action is a reversible one :

$$3HOCl \rightleftharpoons HClO_3 + 2HCl.$$

Experiments were made to ascertain if there is any indication of hypochlorous acid being formed by the action of dilute hydrochloric and chloric acids on each other, but the results were all negative. It has been shown, however, by Foerster (J. Pr. Chem., 1901 (ii.), p. 141), and Sand (*Zeit. physicall. Chem.*, 1904, p. 465), that the action is a reversible one, so that the accelerating action of silver nitrate is quite explicable.

This rapid decomposition of hypochlorous acid in presence of silver nitrate is interesting in connection with the fact that long ago Dancer (*J. Chem. Soc.*, 15, p. 477) gave a method of preparing *hypobromous* acid by the action of bromine water on a solution of silver nitrate, the action being represented as follows :—

$$AgNO_3 + Br_2 + H_2O = AgBr + HOBr + HNO_3.$$

Similarly, there is no doubt that hypochlorous acid is produced when chlorine water is added to a solution of silver nitrate, but this hypochlorous acid decomposes so rapidly in presence of the excess of silver nitrate that this action could not be suggested as a means of preparing the acid.

This considerable difference in the behaviour of hypochlorous and hypobromous acids in presence of a solution of silver is remarkable. Under these conditions the latter acid is much the more stable of the two. If bromine water is shaken up with a sufficient quantity of silver nitrate solution and the liquid filtered from the precipitated silver bromide, it remains clear for days, and gives all the tests for hypobromous acid. But this does slowly decompose, and, if the solution is kept for a long time, silver bromide gradually separates out, forming shining crystals, which for a time float on the surface of the solution.

This difference between the two acids—hypochlorous and hypobromous—is explained by the fact that while the former is only slightly ionised when in solution, the latter is still less so.

Comparison of the Bleaching Action of Chlorine and Hypochlorous Acid.

In former papers the author has frequently expressed the opinion that the general impression that hypochlorous acid is a more active bleaching agent than chlorine is a mistaken one. Further experiments have confirmed this. Many comparative experiments with solutions of chlorine and hypochlorous acid (of the same oxidising strength), and colouring matters of various kinds, have shown practically no cases where the chlorine did not attack the colouring matter more energetically than the hypochlorous acid. Naturally, the bleaching activity of the latter is greatly stimulated by the addition of hydrochloric acid, since this immediately decomposes hypochlorous acid with liberation of chlorine. (This action is later discussed more fully, and it is shown also that hydrochloric acid also stimulates the bleaching action of chlorine water.)* It is remarkable, however, that with moderately strong solutions of hypochlorous acid (say *N*/10 to *N*/20), the bleaching action is stimulated by the addition of other dilute acids, such as sulphuric and nitric, and even phosphoric and acetic acids. But none of them stimulate the action so much as hydrochloric acid, and in the case of very dilute solutions of hypochlorous acid (say *N*/500), the other acids have little or no effect. Since a solution of hypochlorous acid in water is only very slightly ionised, the stimulating effect of sulphuric and nitric acids is doubtless due to the fact that they introduce many more hydrogen ions into the solution

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* An admirable illustration of this difference in activity between chlorine water and hypochlorous acid is to add a few drops of each to separate portions of a dilute solution of indigo-carmine, which is instantly bleached by the former but only very slowly by the latter. The stimulating effect of hydrochloric acid is very evident if a few drops of it are added to the hypochlorous acid before it is mixed with the colouring matter.

If pieces of calico dyed with indigo or turkey red are placed in moderately strong solutions of chlorine and hypochlorous acid of the same oxidising strength, the bleaching is at once seen to proceed more rapidly in the former; but later the hypochlorous acid becomes more active, and may ultimately catch up with the chlorine. The explanation is that as the hypochlorous acid bleaches by giving up oxygen, it leaves hydrochloric acid, which then decomposes some of the remaining hypochlorous acid, liberating chlorine.

Further reference will be made in the next section to the bleaching action of very dilute solutions of chlorine and hypochlorous acid.

The Solution of Chlorine in Water.

More than 50 years ago Williamson held the view that chlorine water contains both hydrochloric and hypochlorous acids, and that the presence of the former was proved by the fact that the solution gave a curdy white precipitate with silver nitrate. He did not state that the action of chlorine upon water was a reversible one, though he probably had this in mind.

Doubtless this view is correct, although in an ordinary saturated solution of chlorine in water the reaction—

$$H_2O + Cl_2 \rightleftharpoons HOCl + HCl$$

does not proceed far in the direction from left to right; a very large proportion of the chlorine is still in the free state, so that comparatively small amounts of hydrochloric and hypochlorous acids are present in the solution. But if the chlorine water is diluted with four or five times its volume of water,* the yellow colour practically disappears, and it might be supposed that the action had proceeded to a considerable extent from left to right. The fact that the colour partially returns on the addition of concentrated hydrochloric acid seems to confirm this. But in the colourless solution the odour of free chlorine persists very strongly.

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* At ordinary temperatures a saturated solution of chlorine in water is a little stronger than $N/10$, so that the diluted solution would be about $N/50$ to $N/60$.

The solution also gives only a slight precipitate with silver nitrate, which, however, rapidly increases in amount. The reaction—

$$H_2O+Cl_2 \rightleftharpoons HOCl+HCl$$

has evidently not proceeded very far from left to right even when the colour has disappeared. The addition of silver nitrate to the solution causes the immediate removal of the hydrochloric acid, and then the reaction proceeds to a finish, all the chlorine disappears, and the solution smells of hypochlorous acid. (For a description of further changes in this solution, see page 71.)

Even when chlorine water is diluted with fifty or a hundred times its volume of water, so that it becomes $N/500$ or $N/1000$, the solution smells distinctly of chlorine, and experiments on the bleaching action of these very dilute solutions also show that they contain a considerable proportion of free chlorine.

With very dilute solutions such as these, experiments on the activity of bleaching of chlorine and hypochlorous acid can be made much more satisfactorily than with stronger solutions, as their action upon such a colouring matter as indigo, for example, is sufficiently slow to enable reliable comparisons to be made. Many comparative experiments have been made (generally using a dilute solution of indigo-sulphonic acid, but also with other colouring matters) with solutions of chlorine and hypochlorous acid diluted to $N/500$, and the chlorine invariably bleaches more rapidly than the hypochlorous acid. Thus, while 20 c.c. of the solution of chlorine bleached a measured volume of the indigo solution in 15 to 20 seconds, the hypochlorous acid always took two or three times as long. Similar differences in the time of bleaching were observed with cochineal, crystal violet, infusion of red rose leaves, and litmus. (The curious action of very dilute chlorine water upon litmus will be described later.)

The bleaching action of dilute chlorine water is considerably accelerated by the addition of hydrochloric acid, which reverses the action of the chlorine on the water, thus liberating more chlorine. Naturally, also, the addition of hydrochloric acid to dilute hypochlorous acid accelerates its bleaching action in the same way. In fact, according to the reversible action—

$$HOCl + HCl \rightleftharpoons H_2O + Cl_2,$$

the addition to hypochlorous acid of just the right amount of hydrochloric acid ought to produce a mixture which would behave exactly like dilute chlorine water. If a solution of *N*/500 hypochlorous acid is mixed with half its volume* of *N*/500 hydrochloric acid, the resulting mixture, in its bleaching action, appears to be absolutely identical with *N*/500 chlorine water mixed with half its volume of water (to bring it to the same volume as the mixed acids). The two solutions bleach at exactly the same rate.

Other acids than hydrochloric do not stimulate the bleaching action of this very dilute hypochlorous acid, as they do with the stronger solutions (see p. 72). In fact, as already pointed out, the solution of indigo used in comparing the times of bleaching was a solution in sulphuric acid.

The results of the comparative bleaching experiments above described leave no doubt that, considered simply as a bleaching agent, chlorine is more active than hypochlorous acid.

S. H. Higgins, however, in various papers (*Chem. Soc. Trans.*, 1912; this journal, 1912, etc.), and more recently in his book on bleaching,† insists that "chlorine is a comparatively weak bleaching agent," and that, in practically all cases of bleaching by hypochlorites, hypochlorous acid is the active agent. His conclusions were drawn from the fact, which he pointed out in 1912, that linen is hardly bleached at all by chlorine. In a paper published by the author in this journal in April, 1912, entitled "The Action of Bleaching Agents on the Colouring Matter of Linen" (see Paper IV., p. 44), it was pointed out that not only has free chlorine very little effect on the colouring matter of linen, but that that colouring matter is equally unaffected by pure hypochlorous acid. The conclusion arrived at was that most of the colouring matter of linen is abnormal in its behaviour with bleaching agents, and that, in order to enable either chlorine or hypochlorous acid to bleach linen, it was necessary to add a certain amount of alkali as well; that, in fact, while neither of those substances alone will bleach linen, a hypochlorite will. As a solution of bleaching powder contains a hypochlorite, it will, naturally, bleach linen.

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* While a normal solution of hydrochloric acid contains 36·5 grms. per litre, a normal solution of hypochlorous acid (measured by its oxidising power) would only contain $\frac{HOCl}{2} = 26{\cdot}25$ grms. per litre, so that a given volume of *N*/500 hydrochloric acid would contain twice as many molecules as the same volume of *N*/500 hypochlorous acid. Consequently, if the two dilute acids were mixed in *equal* volumes, the resulting mixture would not behave like chlorine water, but like chlorine water to which some hydrochloric acid has been added.

† "Bleaching," by S. H. Higgins, 1921. Manchester University Press

In a further paper (this journal, March, 1914) on "The Action of Bleaching Agents on various Natural Colouring Matters" (see Paper V.) it was pointed out that the anomalous behaviour of the colouring matter of linen was shared by a part of the colouring matter of cotton and by the colouring matter of jute. Nearly all the experiments on bleaching which Higgins has described have been done with unbleached linen, and it is plain that little reliance can be placed upon conclusions as to the bleaching activity of chlorine and hypochlorous acid which have been drawn from experiments made with a colouring matter which is unaffected by either of them.

But Higgins continues to state that linen is bleached by hypochlorous acid, and, as a proof of this, he mentions two experiments. In the first he simply added boric acid to a solution of bleaching powder and found that the mixture bleached linen. Now such a mixture would certainly contain both hypochlorous acid and free chlorine, but it would also contain a considerable amount of unaltered calcium hypochlorite, and it is this which bleaches the linen. If the hypochlorous acid were distilled off from the mixture, the pure substance so obtained would not bleach linen.

In his second experiment, Higgins added hydrochloric acid to a solution of bleaching powder until it turned yellow owing to the liberation of chlorine; he then divided the solution into two parts, and to one added precipitated calcium carbonate (to produce hypochlorous acid). He placed some boiled linen in both solutions, and found that the one to which the calcium carbonate had been added had the far greater action (Higgins, this journal, July, 1914). Here again the experiment is rendered worthless as evidence of the superior bleaching power of hypochlorous acid by the fact that pure hypochlorous acid was not used. I have repeated this experiment, but instead of putting the boiled linen into the mixture, the hypochlorous acid was distilled off before use, with the result that the bleaching action was very slight indeed. I found further that if hypochlorous acid, prepared either as just described or by distilling dilute bleaching powder with boric acid, is mixed with a little precipitated calcium carbonate, this has the same effect as the addition of a little alkali (see p. 46), and enables it to bleach linen. It has been pointed out (see page 45) that to enable either chlorine or hypochlorous acid to bleach linen some hypochlorite must be present as well, and it is evident that by the addition of calcium carbonate to either chlorine water or hypochlorous acid the requisite amount of hypochlorite is produced.* Thus the bleaching of the linen in Higgins' experiments is fully and satisfactorily accounted for, and their evidence as to the superior bleaching activity of hypochlorous acid is of no value.

In order to account for some of his results, Higgins has assumed the existence of a form of chlorine more active than the ordinary element, and which he calls " nascent " chlorine. But there is no necessity for such an assumption if we recognise the fact that the colouring matter of linen (together with part of that of cotton), is abnormal in its behaviour to bleaching agents.

The Action of Very Dilute Chlorine Water on Solution o Litmus.

When 40 to 50 c.c. of very dilute chlorine water (5 to 10 c.c. o freshly prepared chlorine water to a litre of water, when the solutio would be from $N/2000$ to $N/1000$) are added to a few c.c. of litmu solution, also freshly made, the liquid at once becomes bright red but in a few seconds the colour changes to purple, and then, i sufficient chlorine water is present, slowly disappears.

The condition of equilibrium in the chlorine water is represente by the equation—

$$H_2O + Cl_2 \quad HOCl + HCl,$$

and the bright red colour which is produced at first is caused by th hydrochloric acid present in the solution, as hypochlorous aci has very little, if any, reddening effect upon litmus. Plainly, whe the colour has changed to purple, the hydrochloric acid has dis appeared from the solution. A probable explanation of this dis appearance of the hydrochloric acid appears to be that the free chlorine in the solution is immediately used up in bleaching some of the litmus, and, as it disappears, the reaction represented above is reversed, and the hydrochloric acid also disappears, producing with the hypochlorous acid more free chlorine, which is used up in bleaching the colouring matter.

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* Since the above was written I have found that if hypochlorous aci (about $N/10$) is shaken up for some time with precipitated calcium carbonate some of the latter is dissolved. If the solution is filtered, the clear liqui gives a considerable precipitate with ammonium oxalate, showing the presenc of calcium in it. Hypochlorous acid has generally been considered too wea an acid to decompose calcium carbonate.

If this explanation is correct, then plainly the time-honoured explanation of the bleaching action of chlorine (the decomposition of water by the chlorine and the consequent formation of hydrochloric acid) cannot be correct—in the case of the bleaching of litmus at any rate. Apparently the chlorine itself acts directly upon the colouring matter.

This experiment also yields an additional proof of the superior bleaching activity of chlorine over hypochlorous acid. If the latter, and not the chlorine, first attacked the colouring matter, and the amount of hypochlorous acid in the solution diminished, this would disturb the equilibrium of the solution in the opposite direction, and so more hydrochloric acid would be produced. Also, hypochlorous acid, when it bleaches, actually yields hydrochloric acid, and this would add still further to the amount of that acid in the solution.

From the results of the experiments described in this paper, it seems plain that the active bleaching properties generally attributed to hypochlorous acid are for the most part imaginary, and are not characteristic of the pure substance itself.

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